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COATED FABRIC FOR USE IN PROTECTIVE CLOTHING

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THE CONNECTICUT HARD RUBBER COMPANY

OCTOBER 1954

WRIGHT AIR DEVELOPMENT CENTER

COATED FABRIC FOR USE IN PROTECTIVE CLOTHING

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THE CONNECTICUT HARD RUBBER COMPANY

OCTOBER 1954

MATERIALS LABORATORY

CONTRACT No. AF33(616)-155

PROJECT No. 7320

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

This report was prepar.d by the Connecticut Hard Rubber Co., New Haven, Connecticut under USAF Contract No. AF 33(616)-155. The contract was initiated under Project No. 7320, (formerly RDO No. 612-13, "Air Force Textile Materials"), and was administered under the direction of the materials Laboratory, Directorate of Research, Wright Air Development Center, with 1st Lt R. W. Logan and 1st Lt C. W. Long acting as project engineers.

..ADC TR 54-93

ABSTRACT

Experimental work leading to the development of a chemically resistant coated fabric, suitable for use in protective clothing for personnel handling various fuels and oxidizers used in guided missiles, is described in this report. The fabric consists of a pigmented blend of polyethylene and Vistanex B-80 calendered on Vinyon Fabric #501, primed with a solution (18% solids) of Vistanex B-80 dispersed in toluol. It possesses good resistance to the action of nitric acid and excellent flexibility throughout a temperature range of -67°F to +157°F when tested in accordance with the procedure outlined in Specification MIL-F-4143 (USAF).

Protective clothing in the form of suits, hoods and gloves, fabricated from the coated material, as well as a number of yards of the fabric itself, has been shipped to the Wright Air Development Center. Since the coated fabric which has been developed is superior to suit materials in present use which exhibit only slight resistance to nitric acid, it is concluded that personnel operating in the field of guided missiles can now be provided with clothing which will offer adequate protection against rocket fuels. It is recommended that the coated fabric be used in the fabrication of all clothing designed for the protection of personnel engaged in handling oxidizers and most rocket fuels.

The coated fabric was developed under Contract No. AF 33(616)-155 at The Connecticut Hard Rubber Company, New Haven, Connecticut, during the period from May 22, 1952 to December 31, 1953.

PUBLICATION REVIEW

This report has been reviewed and is approved.
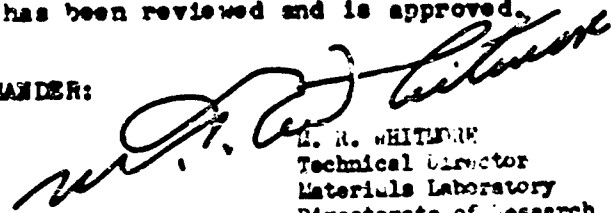
FOR THE COMMANDER:

E. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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INTRODUCTION

As the program of activities concerned with guided missiles
becomes wider in scope, the demand for trained personnel
grows ever greater, and with their increase in number comes
a need for more effective means to protect them from the
hazards encountered in the field. The protective clothing
in present use, consisting of glass fabric coated with
polyvinyl chloride, affords only a slight degree of protection,
especially in the case of rocket fuels such as fuming nitric
acid. hence, the task was assigned to develop a material
suitable for the fabrication of clothing, which, among other
requirements, would be resistant to the action of white
fuming nitric acid and would be flexible throughout a tem-
perature range of -67°F to +157°F.

For the development of a chemically resistant coated fabric,
the following polymers were designated as being of special
interest to Wright Field: polyethylene, polyisobutylene,
polytetrafluoroethylene and polymonochlorotrifluoroethylene.
Since polytetrafluoroethylene (Teflon) and polymonochloro-
trifluoroethylene (Kel-F) are outstanding in their resistance
to chemical attack, the initial experimental work under the
subject contract was concerned with an investigation of
commercial Teflon and Kel-F films, as well as those cast
from solvent dispersions on various types of glass fabrics,
and fused to make a continuous film. In conjunction with
these experiments, an investigation was made of polyethylene-
polyisobutylene (Vistanex) films cast from solution, together
with press-molded films of polyethylene-polyisobutylene blends.
Another experimental step was an evaluation of Kel-F-glass
fabric-silicone rubber laminates as well as products result-
ing from the lamination of plasticized, extruded Kel-F film
to Fiberglas.

While plasticized Kel-F film was found to provide an outstand-
ing degree of protection against fuming nitric acid, much
superior to that of polyethylene-polyisobutylene blends
which were the next best, suit materials obtained by coating
glass fabrics with Kel-F dispersions had an inherent stiffness
which was lessened to a certain extent but never completely
eliminated. Many of the difficulties with fluorocarbon-
coated fabrics arise from the necessity of using Fiberglas
as the supporting fabric. No other known fabric has sufficient
heat-resistance to withstand the fusion temperatures required
in the preparation of coatings from fluorocarbon dispersions.
Problems concerned with glass fabrics are poor flex life,
the possibility of irritation to the skin, and the high
expense involved in its use.

The loss of flexibility which results from coating with Kel-F can be easily explained by a consideration of the mechanical properties of Fiberglas. Fiberglas is made from microdiameter glass filaments which are twisted into thread and then woven into fabric. The glass filaments, although supple because of their extreme thinness, are still glass and by their very nature cannot withstand much bending or flexing without breaking. Hence, the flexibility of glass fabrics is a result of the filaments slipping and sliding past each other. The application and fusion of the relatively inflexible Kel-F to the fabric locks these filaments in place, limits their ability to slide past one another, and therefore the fabric becomes stiff and brittle.

When maximum acid protection had been obtained with fluorocarbon-coated fabrics, a conference was held with personnel of Wright Air Development Center (December 9, 1952). Here, the potentialities and drawbacks of fluorocarbon constructions were discussed. It was decided that in view of the relatively short exposure time anticipated in actual use in protective clothing, absolute acid-resistance should be compromised for greater flexibility and wearer comfort. It was suggested at this meeting that the remainder of the time on the contract be concentrated on polyethylene-polyisobutylene blends.

Subsequent work on blends of polyethylene and polyisobutylene, calendered on Vinyon, indicated that a pigmented blend of sixty parts polyisobutylene (Vistanex B-80) and forty parts polyethylene provided resistance to nitric acid on the order of forty hours, which is markedly superior to that of present protective clothing. The flexibility of the fabric is excellent, approaching that of normal wearing apparel, and flexibility is maintained throughout a temperature range of -67°F to +157°F. Moreover, the fabric can be processed with ease on existing calendering equipment.

EXPERIMENTAL WORK

A. Target Requirements and Conformity of Coated Fabric to Specification MIL-F-4143 (USAF)

Experimental work under the present contract (AF 33(616)-155) has been carried out with the objective of developing a coated fabric for use in protective clothing for personnel handling various oxidizing agents and fuels used in guided missiles. The protective clothing in present use, consisting of a base fabric coated with polyvinyl chloride, offers only slight resistance to nitric acid.

As the program on guided missiles expands, the shortage of trained personnel operating in the field becomes more and more critical. Consequently, less experienced people are handling highly corrosive rocket fuels, and the danger of accidents is increasing proportionately. There is therefore a distinct need for suitable protection against rocket fuels, especially fuming nitric acid.

The desired coated fabric is to meet the following requirements, listed in Exhibit "A" of the subject contract.

A. The coated fabric should be resistant to the following chemicals:

1. Red Fuming Nitric Acid (6$\frac{1}{2}$% NO_2)
2. Mixed Acids (Fuming Sulfuric and Red Fuming Nitric)
3. Hydrogen Peroxide (90%)
4. Liquid Oxygen
5. Furfuryl Alcohol
6. Aniline and Furfuryl Alcohol (70%-30%)
7. Ethyl Alcohol (Commercial)
8. Aniline
9. Monoethylaniline
10. Hydrazine (94%)
11. Anhydrous Ammonia
12. Ammonia (Commercial)

B. The fabric shall be flexible throughout a temperature range of -67°F to +157°F, when tested in accordance with the procedure outlined in Specification MIL-F-4143 (USAF).

C. The fabric shall have the best possible abrasion resistance, tear strength and breaking strength, and shall not cause dermatitis.

The coating which has been developed for use when applied to a base fabric is a pigmented blend of polyethylene and Vistanex B-80. The base fabric selected is Vinyon 501* (4 oz/yd2). Samples of the blend, continuously calendered onto Vinyon fabric, primed with a solution (10% solids) of Vistanex B-80 dispersed in toluol, have been evaluated and were found to meet the requirements for the coated fabric. There should be no cause for dermatitis. Complete data on the fabric are tabulated below.

Uncoated Fabric

Vinyon Fabric (#501, Flightex Corporation)
Count: 50 x 50
Weight: 3.70 oz/sq yd.
Thickness: .007 in.
Color: Natural, undyed (yellow)
Weave: Plain

Primer

10% solids Vistanex B-80
dispersed in toluol, spread on one side of fabric.
Weight: 1.01 oz/sq yd.
Thickness: .001 in. approximately
Colorless

Coating

60 parts Vistanex B-80
and 40 parts polyethylene (Alathon A)
with 5 parts Titanox A and 2 parts stearic acid,
calendered on one side of fabric
Weight: 6.49 oz/sq yd.
Thickness: .008 in.
Color: white

Finished Fabric

Weight: 11.2 oz/sq yd.
Thickness: .016 in.
Color: Outer surface, white
       Nether surface, yellow

*It is to be noted that Vinyon 501 is 100% Vinyon (polyvinyl chloride) and not a mixture of polyvinyl chloride and acrylonitrile, which is known as Vinyon N.

Resistance to penetration of nitric
acid, hours exposure before passage of 2.5 grams

HNO_3/sq. meter	40 hours
Low-Temperature Flexibility 3.5 hours at -80°F	No cracking, checking or stiffness
Flame-Resistance	Burns, but difficult to start
Tear Strength, lbs/in. avg. tongue method	Warp-5.0 lbs. Fill-6.0 lbs.
Adhesion Pull, 2 in/min lbs/in. (Scott)	Warp-Coating ruptures in excess of an average of 2.72 lbs. (Peak-3.4)
	Fill-Coating ruptures in excess of an average of .60 lbs. (Peak-.8)
(b) Crank Test,[1] 50 turns	Pass
(c) DuPont Scrub Test [2]	Withstood 200 cycles
Breaking Strength lbs/in. Average (Scott)	Warp-79.5 lbs. Fill-67.2 lbs.
Heat Stability 2 hrs. @ 153°F ± 2° 2 hrs. @ 200°F ± 2°	No decomposition or cracking on flexing

[1] Crank Test - The coated fabric is held firmly between the thumb and forefinger of each hand. A space of approximately 1 inch is maintained between the hands. The hands are then moved alternately forward and backward. The number of cycles needed to cause a breakdown of the coating is then noted, which indicates resistance to flexing. If the coated fabric survives fifty cycles, it is considered to have passed the test successfully.

[2] DuPont Scrub Test - The DuPont Scrub Test, a mechanized version of the Crank Test, was developed by the Fabrics and Finishes Department of DuPont to measure the "scrub resistance" of a coated fabric. The fabric is placed in clamps which move back and forth in opposite directions at a rate of 110 cycles per minute, which gives the scrubbing action to the specimen. The number of strokes is recorded. When a breakdown of coating is noted, the test is considered complete. (See The Vanderbilt Rubber Handbook. Ninth Edition. R. T. Vanderbilt Company, New York, 1948. pp. 433-435.

The general resistance of the coated fabric to the action of
various oxidizing agents and fuels which might be used in
guided missiles, was determined. Favorable results were
obtained.

B. Polyethylene-Vistanex Blends

The coated fabric which has been developed under the subject contract is a pigmented blend of polyeth..ene and Vistanex. This section of the final report covers in considerable detail the experimental work leading to the final product.

Personnel of Wright Field supplied for our examination a sample of Orlon, coated with a compounded mixture of polyethylene and Vistanex which was pigmented with carbon black. Wright Field had conducted permeability tests on various materials of possible use for protective clothing, and the polyethylene-Vistanex blend had shown some promise. Tests in our laboratory showed that the sample supplied by Wright Field had relatively poor resistance to the permeation of white fuming nitric acid, particularly in comparison with that of plasticized Kel-F film. Steps were taken, however, to prepare films of uncompounded polyethylene-Vistanex blends for evaluation as nitric acid barriers. It was discovered that mixtures containing no carbon black showed nitric acid resistance far superior to that of the material supplied by Wright Field. Further work revealed that carbon black was responsible for the lack of resistance to the permeation of nitric acid. A very definite synergism was found to exist between polyethylene and Vistanex, since either material, by itself, exhibited only fair resistance to nitric acid. (Some work has been done on butyl-Vistanex blends for use in protective clothing, which is reported by A. R. Allison, as noted in the Literature Survey, 4. Chemically Resistant Protective Clothing.)

Polyethylene-Vistanex blends were investigated further. Work at this stage was largely concerned with the development of improved techniques for preparing solution-cast films and a preliminary examination of films prepared by press-molding. Press-molded polyethylene-Vistanex films were found to exhibit a resistance to nitric acid, definitely superior to that of solution-cast films of similar composition. This indicated that a calendered coating would surpass a solution coating. Therefore the fabrication of coated materials by calendering techniques was investigated, with particular emphasis on such requisites as calenderability, adhesion, flame-resistance, freedom from blocking, crease-resistance, resistance to oxidizing agents and fuels, and the processing of a colored fabric. The effects of pigments and fillers were investigated. While various compounds were found to improve calenderability and to reduce blocking, acid-resistance was also reduced.

Since chlorosulfonated polyethylene (Hypalon S-2) offered promise as a substitute for polyethylene, Vistanex-Hypalon films were press-molded for evaluation as nitric acid barriers. Acid-resistance was found to be markedly inferior to that of press-molded polyethylene-Vistanex films.

When the pigmented blend of polyethylene and Vistanex, calendered on Vinyon, was believed to fulfill all necessary requirements, a full-scale run on a production calender was made. The coated fabric obtained by the calendering of the polyethylene-Vistanex blend on Vinyon was used in the fabrication of protective clothing such as suits, hoods and gloves. A study was made of suitable means for the protection of seams.

1. Solution-Cast Films

The initial evaluation of solution-cast polyethylene-Vistanex films was worthy of further investigation. On the basis of exposure for a relatively short time, a good degree of acid-resistance was obtained and the flexibility of the films was excellent. The procedure (Procedure A, Appendix) for determining permeability to fuming nitric acid consisted in using a specimen as a diaphragm in a U-shaped cell which was divided into two sections at the bottom of the "U". Conductivity water was put in half of the cell, and white fuming nitric acid in the other. The pH of the conductivity water was measured at intervals, and the permeability was calculated from the dimensions of the system. Figure 1 is a calibration curve of the test cell used in obtaining nitric acid penetration data. The calibration curve relates the measured pH to the permeation rate in grams per square meter for white fuming nitric acid through a test membrane. The experimental setup is pictured in Figures 2 and 3. The test is the general application of the theory of diffusion (see Literature Survey, 1. Permeability). The procedure was developed by the Naval Air Rocket Test Station.

Films cast (Procedure B, Appendix) from various blends of polyisobutylene (Vistanex) and polyethylene for evaluation as fuming nitric acid barriers showed maximum resistance in the range of 70 parts of polyethylene and 30 parts of polyisobutylene, with a decrease in resistance as 100 parts of polyethylene was reached (Figure 4). Permeability data on a solution-cast film comprised of 70 parts of polyethylene and 30 parts of Vistanex B-80 are tabulated in the Appendix Table 1,1. Vistanex, itself, has very little nitric acid
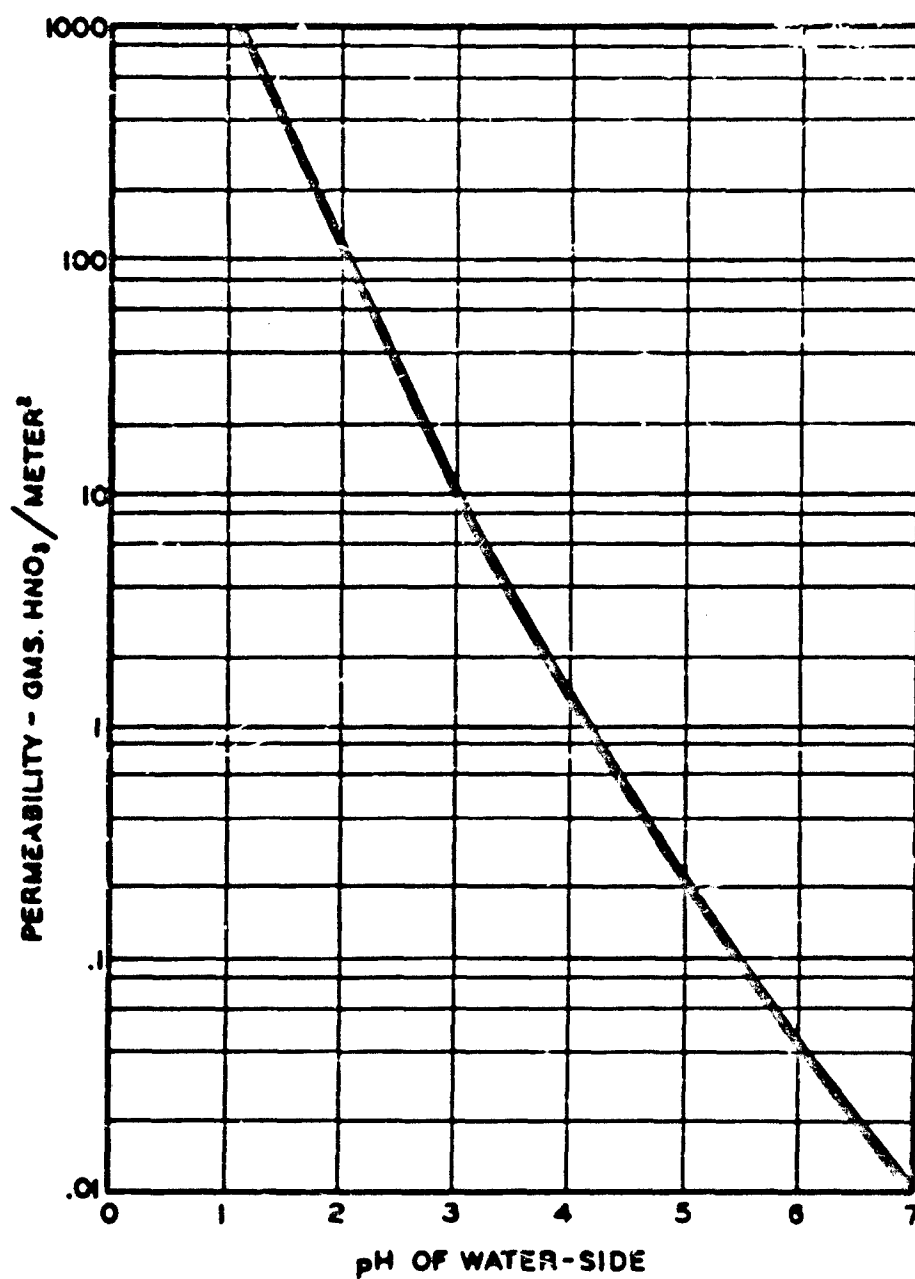
FIG.1- CALIBRATION CURVE OF TEST CELL

FIG. 2 – CLOSE-UP OF NITRIC ACID PERMEABILITY, TEST CELL AND pH METER.
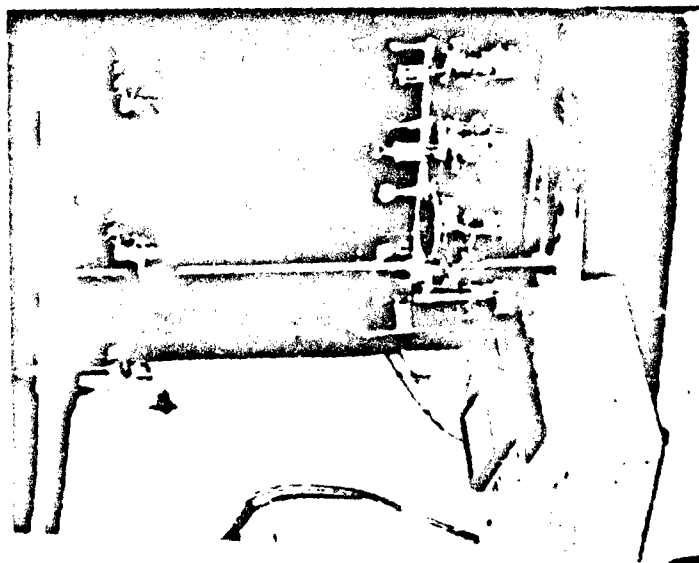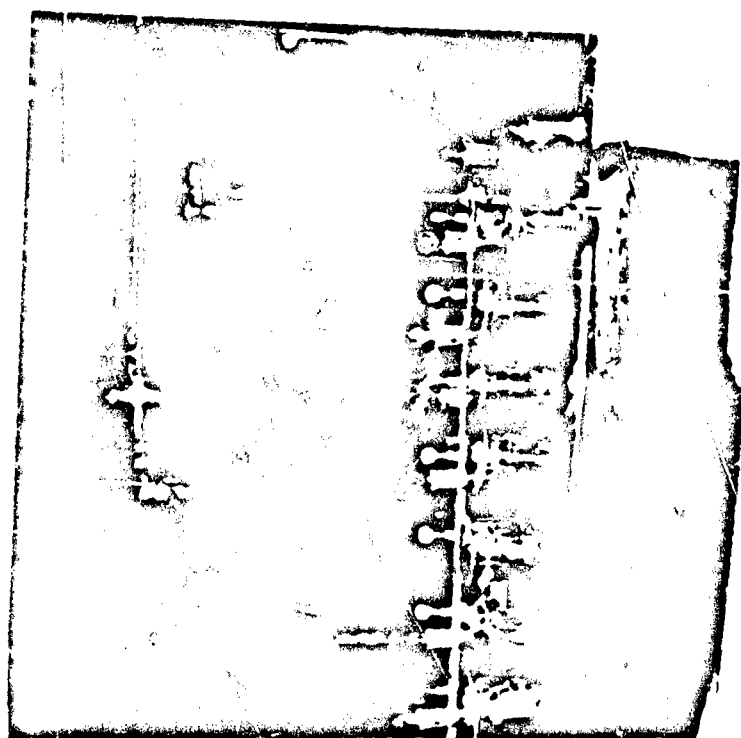
FIG. 3 – ASSEMBLY OF NITRIC ACID PERMEABILITY TEST CELLS
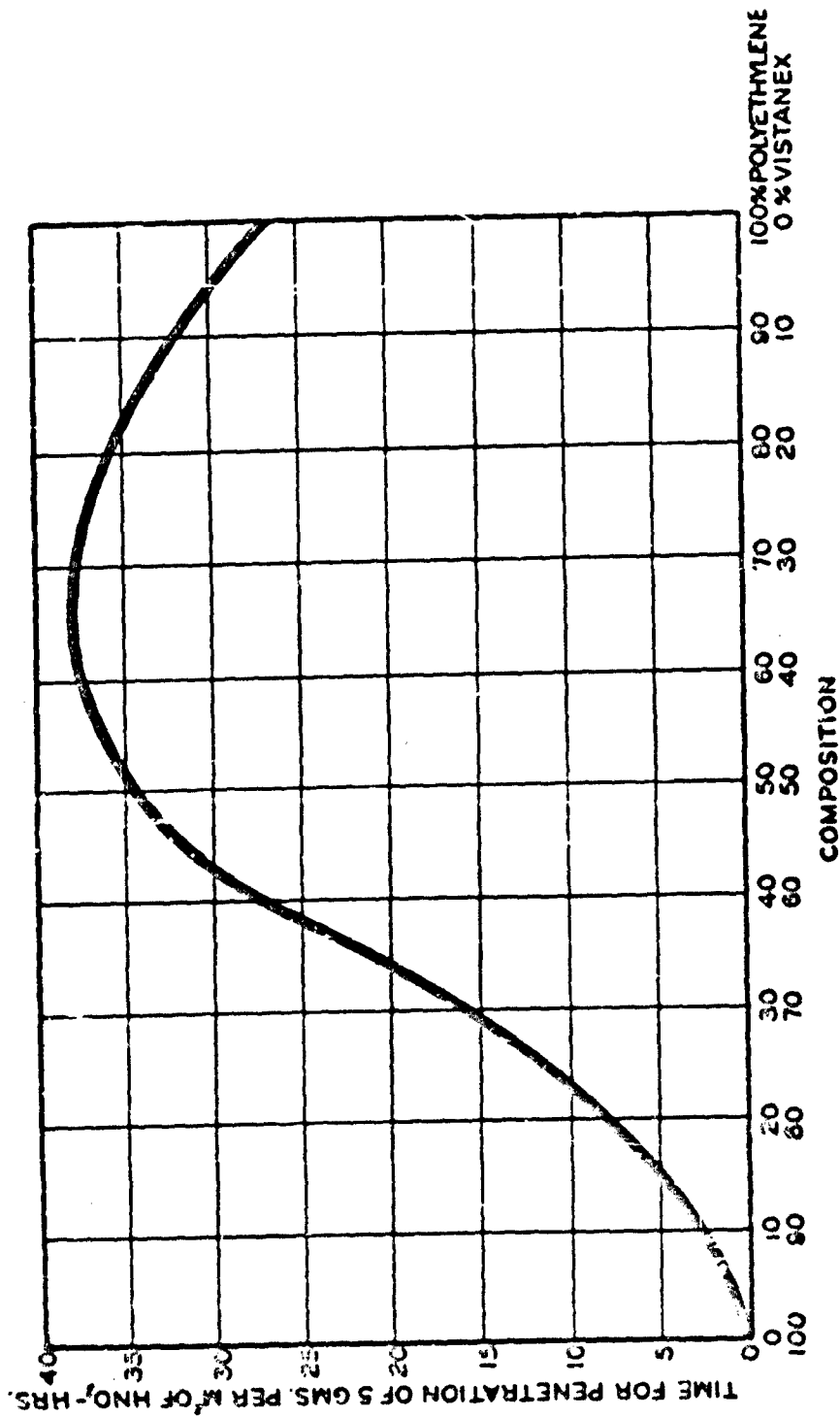
FIG. 4 – NITRIC ACID PENETRATION VS. COMPOSITION
VISTANEX - POLYETHYLENE BLENDS

resistance. However, it serves as an excellent modifying
agent to increase the flexibility of polyethylene and render
it a more suitable fabric-coating material, without reducing
its acid-resistance. Polyethylene film, itself, proved to
be a very poor nitric acid barrier, either when solution-
cast (Procedure C, Appendix) or when calendered (Procedure
D. Appendix), as will be noted in Figure 5 and in the
Appendix, Table 1,ii and iii. Figure 6 is a comparison
of the rates of penetration of nitric acid into various
Vistanex-polyethylene blends and into samples of the suit
material submitted by Wright Field. The data upon which
these curves are based may be found in the Appendix,
Table 1, i, iii, and iv through vii.

It was found that the difficulties of solution-casting
polyethylene-Vistanex films are primarily due to the insolu-
bility of polyethylene in toluene at lower temperatures.
Large precipitated particles of polyethylene in the finished
film are found to decrease the resistance of the film to acid-
permeation. A second difficulty is that of residual solvent,
causing failure of some films after relatively short exposure
(10 to 20 hrs.) to fuming nitric acid. Since toluene is not
resistant to nitric acid, any small amount of solvent present
in the film is detrimental to acid-resistance. It was
discovered that after drying for a long time at about 150°F,
the acid-resistance of solution-cast films improved. However,
while it is possible to remove the greater part of the solvent
by oven-drying, the last small fraction of solvent will per-
sist for months.

With the development of improved techniques, a second series
of films was prepared (Procedure E, Appendix) from various
blends of polyethylene and Vistanex by the solution-casting
method, followed by extending drying. Films, .006 to .007
in. thick, were subjected to acid-permeability tests.
Permeability of the individual films is shown in Figure 7.
The data upon which these curves are based may be found in
the Appendix, Table 2, i through x.

Examination of Figure 7 reveals that extended oven-drying
does have a favorable effect on solution-cast films. There
was marked improvement in the impermeability of this series
of solution-cast films over those prepared earlier. It is
apparent that Film #132 comprised of 50 parts polyethylene
and 50 parts Vistanex B-80 was most resistant to the penetra-
tion of fuming nitric acid. However, in comparing impermeabil-
ity data of solution-cast films with those of press-molded
films, it will be seen that solution-cast films still fall
far short of desirable resistance to nitric acid.

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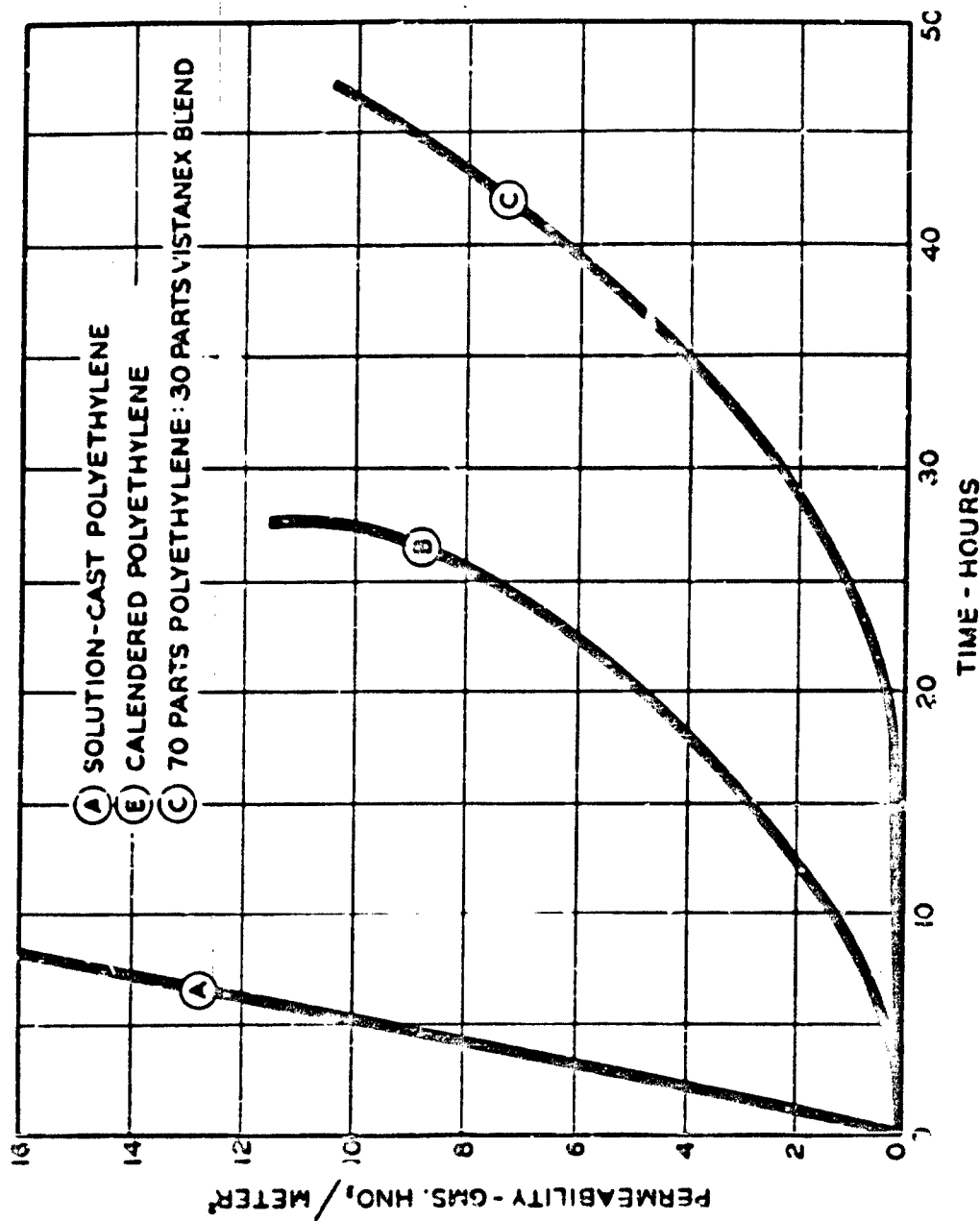
FIG. 5 - NITRIC ACID PENETRATION VS. TIME, VARIOUS FILMS

Legend:
- (A) SOLUTION-CAST POLYETHYLENE
- (B) CALENDERED POLYETHYLENE
- (C) 70 PARTS POLYETHYLENE : 30 PARTS VISTANEX BLEND

Y-axis: PERMEABILITY - GMS. HNO_3/METER^2

X-axis: TIME - HOURS
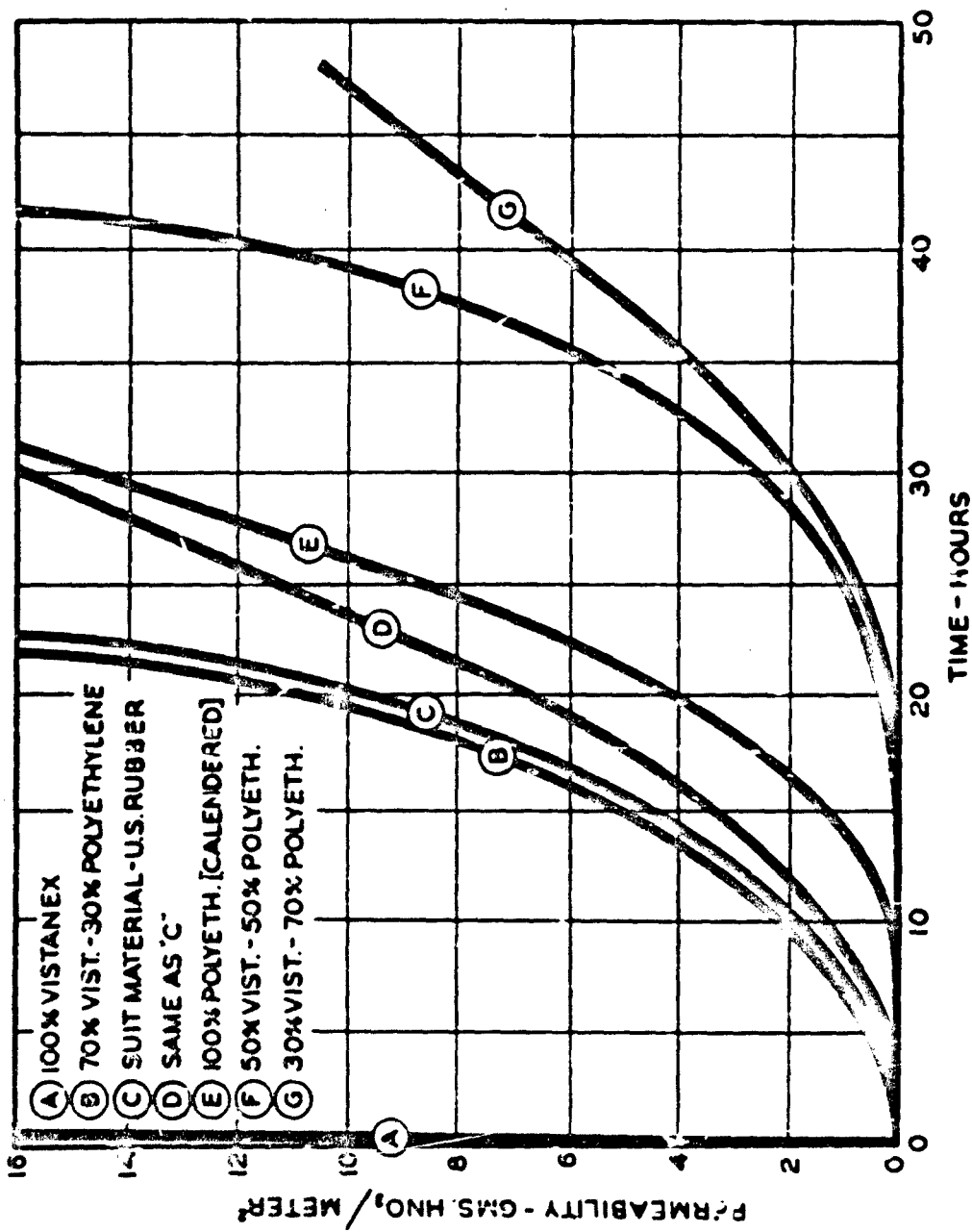
FIG. 6-NITRIC ACID PENETRATION VS. TIME,
VISTANEX - POLYETHYLENE BLENDS.

Legend:
(A) 100% VISTANEX
(B) 70% VIST. - 30% POLYETHYLENE
(C) SUIT MATERIAL - U.S. RUBBER
(D) SAME AS 'C'
(E) 100% POLYETH. (CALENDERED)
(F) 50% VIST. - 50% POLYETH.
(G) 30% VIST. - 70% POLYETH.

X-axis: TIME - HOURS
Y-axis: PERMEABILITY - GMS. HNO_3 / $METER^2$
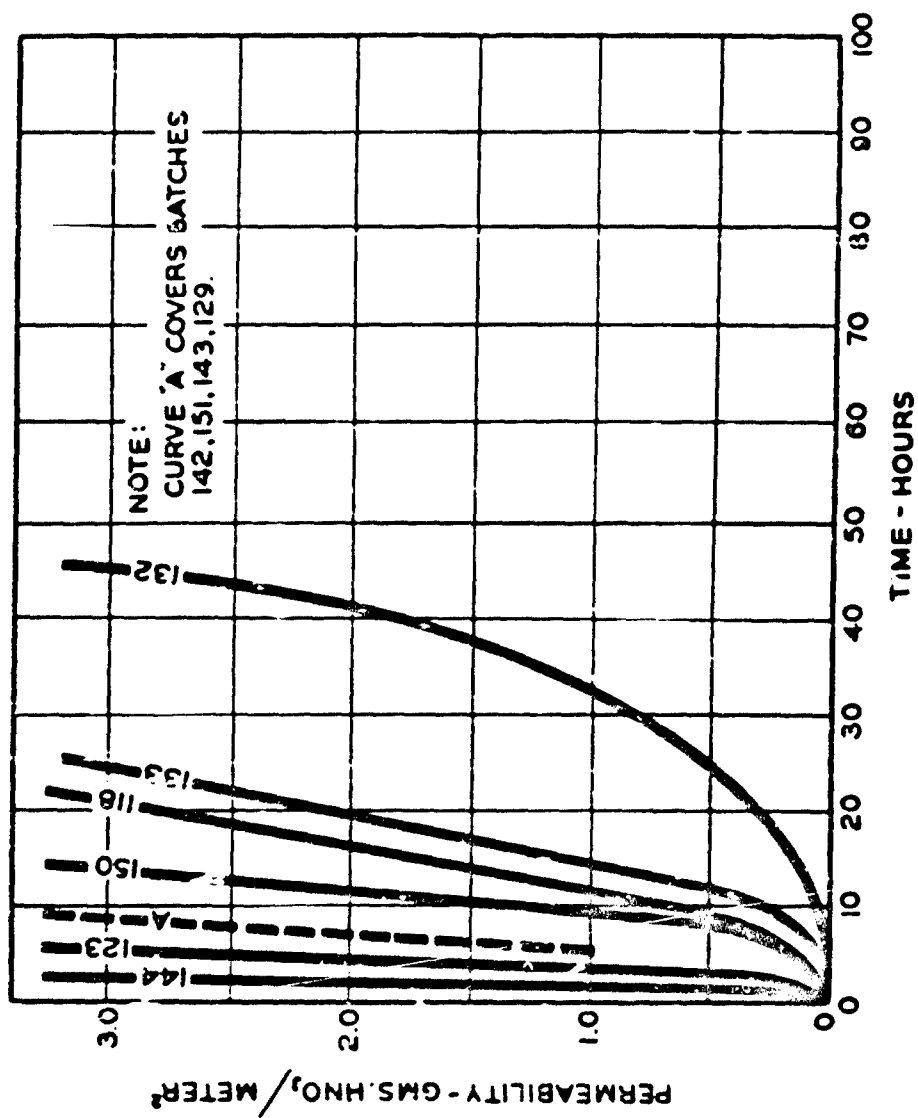
FIG. 7-NITRIC ACID PERMEABILITY OF SOLUTION-CAST
POLYETHYLENE -VISTANEX FILMS [006"-007"]

2. Press-Molded Films

Press-molding is a laboratory procedure for the preparation of simulated calendered coatings, which is used to avoid the difficulties inherent in calendering. By means of this method, a number of hand samples can be prepared in a minimum of time. In an evaluation of press-molded films of the same polyethylene-Vistanex blends, the results of acid-resistance tests were much more promising. The press-molded films differed from the solution-cast films not only in their superior resistance to nitric acid but also in the optimum ratio of Vistanex to polyethylene. Excellent nitric acid resistance was obtained with polyethylene-Vistanex B-80 blends in the range of 40 parts polyethylene and 60 parts Vistanex B-80, to 20 parts polyethylene and 80 parts Vistanex B-80 in thicknesses of eight mils, or more. Extremely good flexibility was noted.

A complete series of films was prepared (Procedure F, Appendix) from various blends of polyethylene and Vistanex by the press-molding method. Films, .008 in. thick, were subjected to acid-permeability tests. Permeability of the individual films is shown in Figure 8. The data upon which these curves are based may be found in the Appendix, Table 3, i through xi. Data showing the effect of concentration of components on the acid-resistance of press-molded films as compared with solution-cast films are shown in Figure 9.

Film #164, comprised of 20 parts polyethylene and 80 parts Vistanex B-80, displayed such resistance to nitric acid that over 300 hours of exposure were required before 2.5 grams of nitric acid permeated the film. This degree of resistance was second only to plasticized Kel-F film, which will be discussed in a later section of this report.

A study was made of the effect of higher molecular weight Vistanex on the acid-resistance of the blends. Press-molded films prepared, as in Procedure F, Appendix, from various blends of polyethylene and Vistanex B-100 revealed a resistance to nitric acid of the same order of magnitude as that of films containing Vistanex b-80 (Appendix, Table 4, i through v). In the section of this report dealing with calenderability of experimental fabrics coated with blends of polyethylene-Vistanex, it will be shown that higher molecular weight Vistanex reduced calenderability. Batches containing even relatively small proportions of Vistanex B-100 were so nervy that they could not be calendered on fabrics at all.
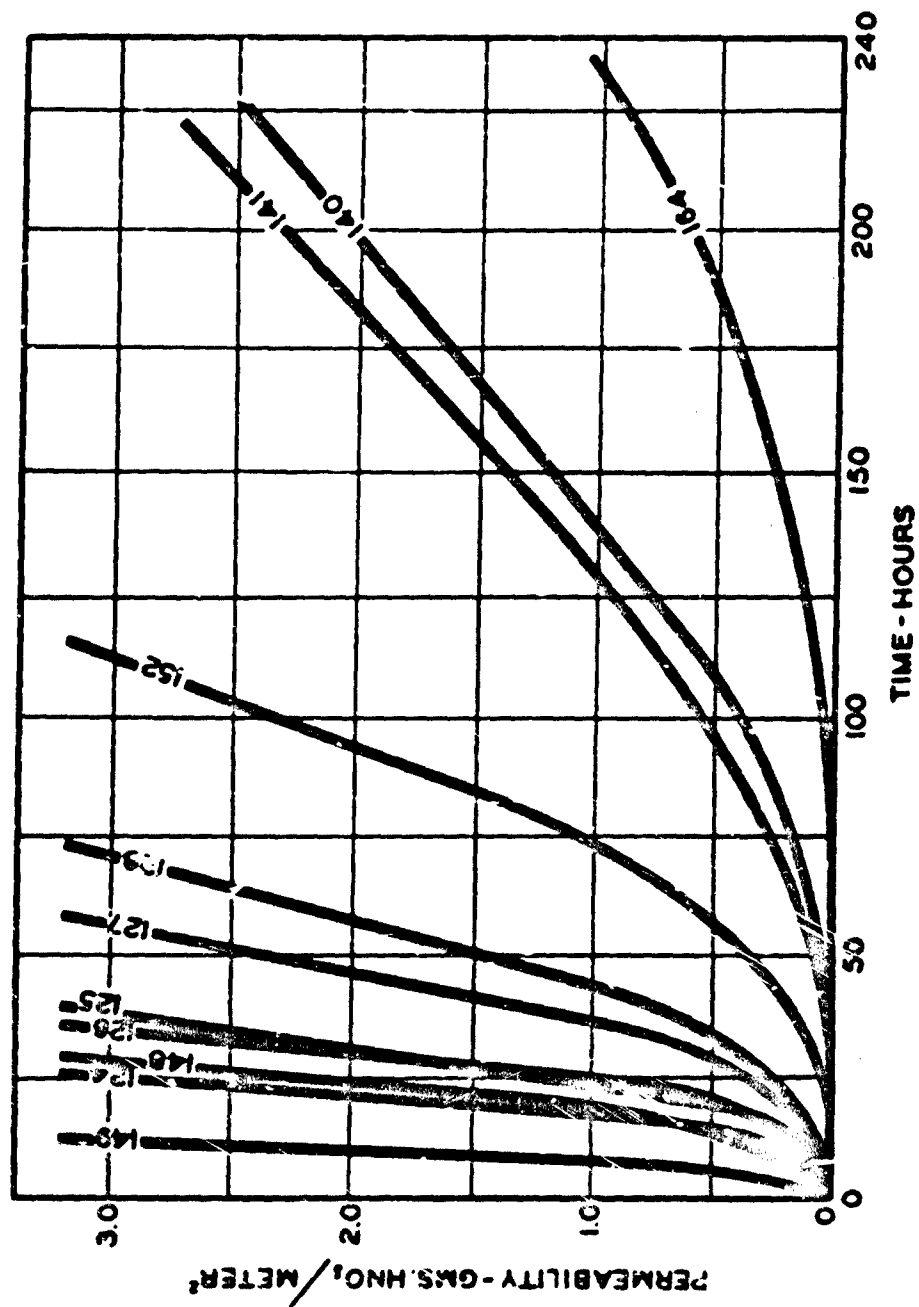
FIG.8-NITRIC ACID PERMEABILITY OF PRESS-MOLDED
POLYETHYLENE -VISTANEX FILMS [.008"]

PERMEABILITY - GMS. HNO₃/METER²

TIME - HOURS
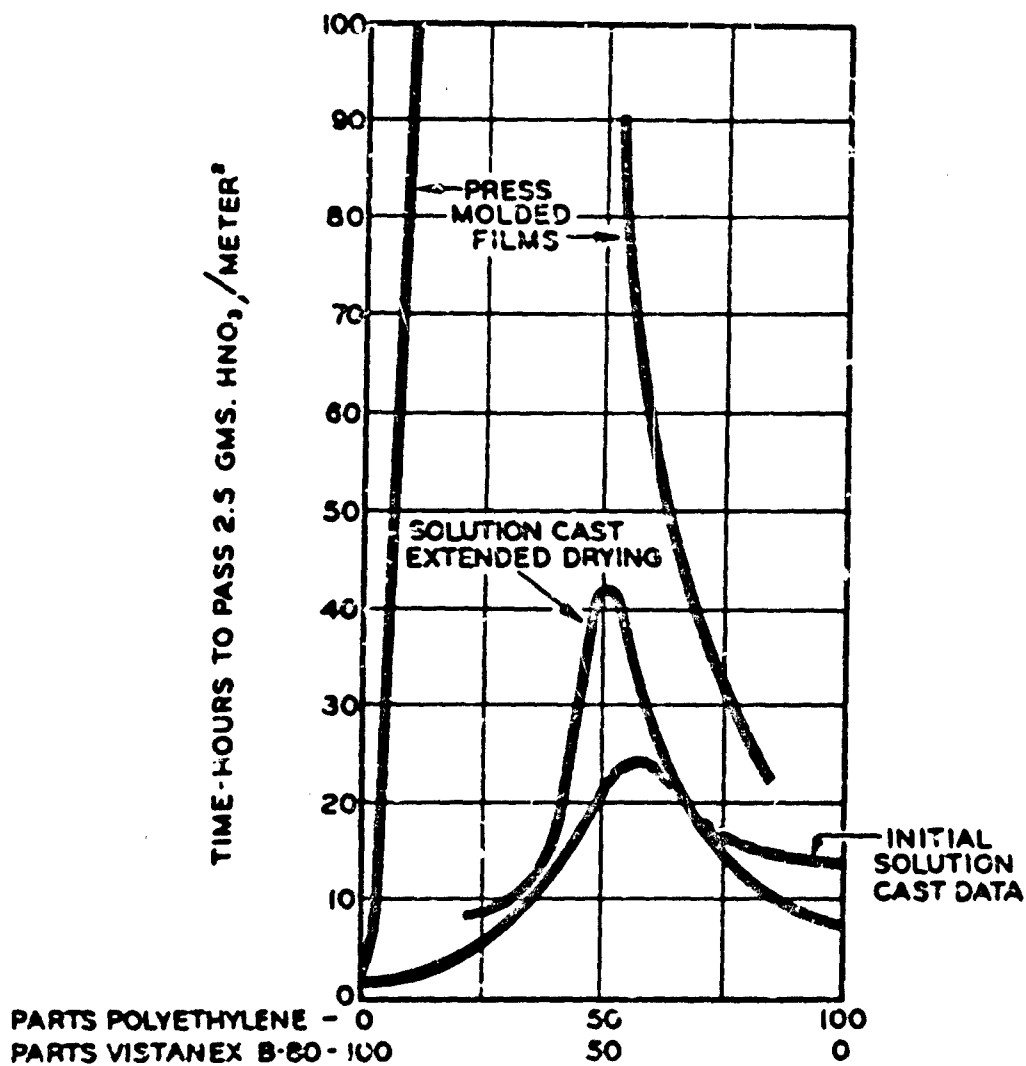
FIG. 9 - COMPARISON BETWEEN PRESS-MOLDED
AND SOLUTION-CAST FILMS

NITRIC ACID PERMEABILITY VS. COMPOSITION.

It was discovered that press-molded films containing high molecular weight Vistanex B-120 showed some improvement in acid-resistance over those containing Vistanex B-80. Films prepared from various blends of polyethylene-Vistanex B-120 showed some reduction in acid-penetration for a period of time up to about seventy-five hours (Appendix, Table 4,vi through ix) with increasing proportions of Vistanex B-120. The permeability of a film, .008 in. thick, comprised of 50 parts polyethylene and 50 parts Vistanex B-120 (Appendix, Table 4,vii), in comparison with that obtained with the corresponding blend of polyethylene and Vistanex B-80 (Appendix, Table 3,vi), is indicated in Figure 10.

However, while high molecular weight Vistanex B-120 provides some improvement in resistance to acid-penetration, it also leads to an increase in the nerve of a given blend. Poly-ethylene-Vistanex B-120 blends were extremely nervy, which made processing difficult. A great deal of energy was re-quired to sheet into films, batches containing as little as 40 parts Vistanex B-100 and B-120. Again, it was dis-covered that it was impossible to obtain calendered samples of coated fabrics with the B-120 blend. The use of Vistanex of a higher molecular weight than that of Vistanex B-80 was therefore considered to be impracticable.

Vistanex-Hypalon Films

Since Hypalon S-2 (chlorosulfonated polyethylene) was of interest as a possible substitute for polyethylene, two sets of films .008 inch thick, were prepared by the press-molding method from various blends of Hypalon S-2 and Vistanex B-80, for evaluation as nitric acid barriers. One set was mixed and pressed in the same manner used with the polyethylene-Vistanex blends. To the other set, two percent of zinc oxide, based on the Hypalon, was added to activate the cure of the Hypalon. The acid-resistance of the straight Vistanex-Hypalon S-2 films as well as the films containing zinc oxide was markedly inferior to that of polyethylene-Vistanex films (Appendix, Table 5,i through xiii).

In Figure 11, acid-permeability of films obtained from various Vistanex-Hypalon S-2 blends is plotted as a function of blend composition. For purposes of comparison, some of the poly-ethylene-Vistanex data are also plotted. As indicated in Figure 11, Vistanex-Hypalon S-2 blends show only slight resistance to nitric acid penetration. The addition of zinc oxide gives no substantial improvement.
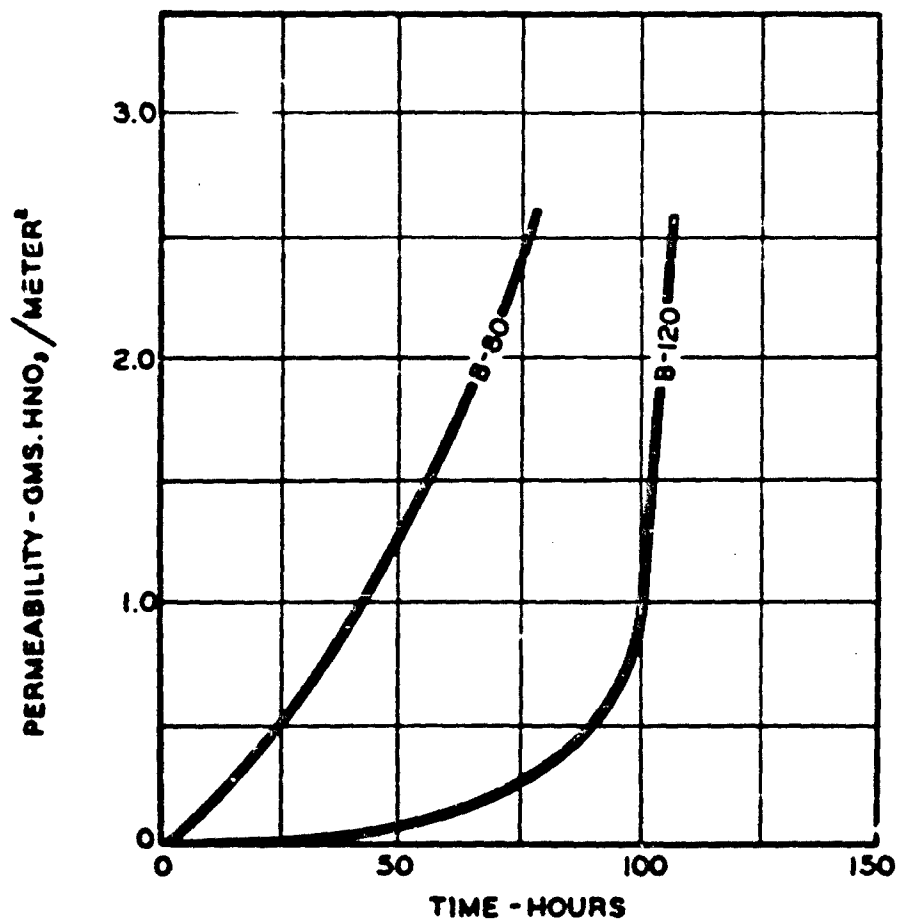
FIG.IO-THE EFFECT OF THE MOLECULAR WEIGHT
OF VISTANEX ON THE NITRIC ACID PERM-
EABILITY OF PRESS-MOLDED POLYETHYLENE-
VISTANEX FILMS [.008"]

50 PARTS POLYETHYLENE - 50 PARTS VISTANEX.
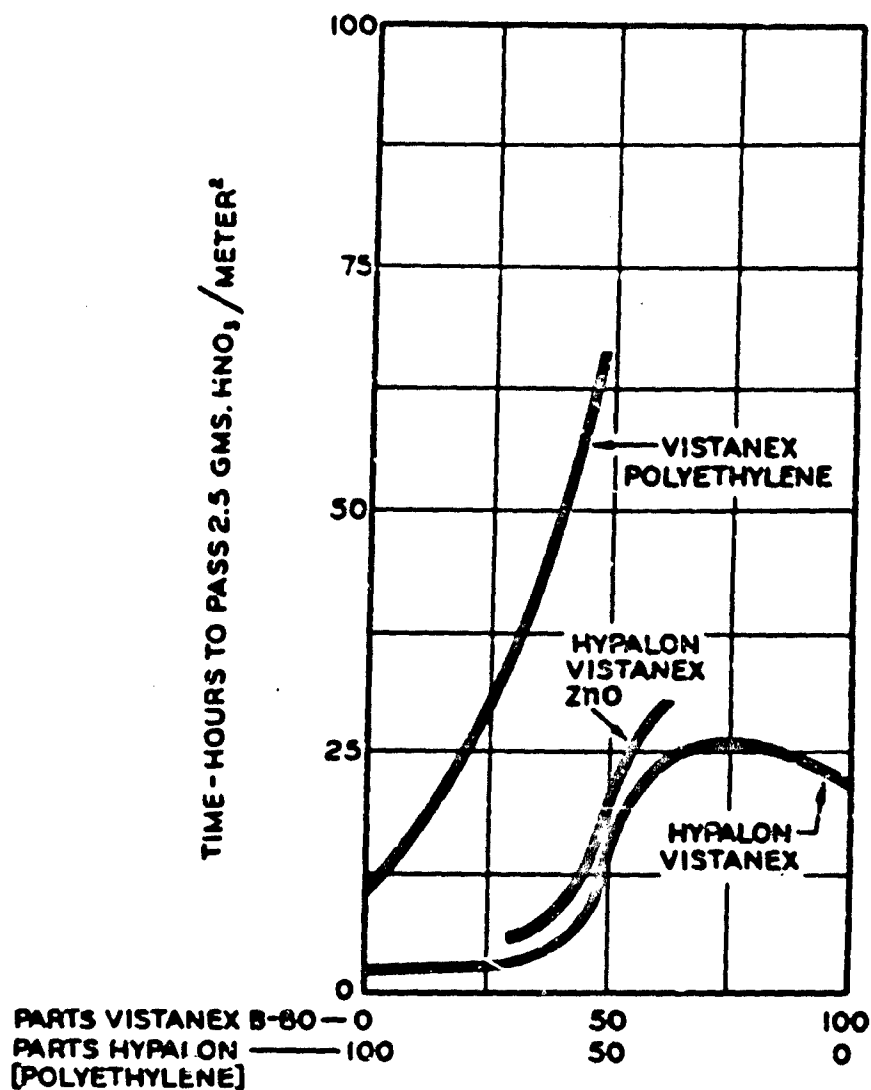
FIG.11 - THE EFFECT OF BLEND COMPOSITION ON
THE NITRIC ACID PERMEABILITY OF PRESS
MOLDED HYPALON-VISTANEX B-80 FILMS-.008"

Several films were also prepared from various blends of Hypalon S-2 and polyethylene, in the same manner as above. These, too, showed negligible resistance to nitric acid (Appendix, Table 5, xiv through xvi).

3. Experimental Coated Fabrics

a. Calenderability Studies on Pilot-Plant Calender

In determining the optimum combination of polyethylene and Vistanex for the development of a coated fabric which would satisfy the requirements of the contract, it was found that one important variable was the composition which could be easily calendered.

The initial method used in calendering the blends on the base fabric was the standard calender-coating procedure whereby a length of fabric is fed continuously through the calender rolls. The relative calenderability of batches was judged on the basis of pickup and ease of calendering. Most of the blends evaluated by the use of this method were adjudged "poor calendering".

Until the techniques of continuous coating could be developed, it was necessary to use a second method to obtain small samples (approximately 4 in. by 4 in.) for evaluation of acid-resistance. In this method, after the blend was banded smoothly on the middle roll of the calender, a sample of fabric (approximately 6 in. by 12 in.) was fed into the bite between the two lower rolls. When the fabric was about halfway through the rolls, the calender was stopped and the small sample of coated fabric was loosened from the middle roll. When the calender was started again, the whole sample could easily be pulled free. For purposes of laboratory evaluation of samples for nitric acid resistance, the "start and stop" method of calender-coating was adequate.

Preliminary work on the calender-coating of Dynel and Vinyon Fabric #501 was carried out with blends of polyethylene and Vistanex B-80. In one case, Vistanex B-100 was used. The middle roll of the calender was heated to 235°F in all runs. Calenderability on Vinyon, as affected by variation in the molecular weight of Vistanex and by the presence of pigments, is tabulated on the following page.

COATING CHARACTERISTICS OF VARIOUS POLYETHYLENE-
VISTANEX BLENDS ON VINYON

Batch Composition	Pickup	Adhesion
50 parts Vistanex B-80 50 parts Alathon A	Good	Good
60 parts Vistanex B-80 40 parts Alathon A	Good	Good
70 parts Vistanex B-80 30 parts Alathon A	Fair	Fair
80 parts Vistanex B-80 20 parts Alathon A	Poor	Poor
50 parts Vistanex B-100 50 parts Alathon A	Poor	Poor
13 parts Vistanex B-80 54 parts Alathon A 33 parts Titanox A	Fair	Fair
27 parts Vistanex B-80 27 parts Alathon A 46 parts Hi-Sil	Fair	Fair

Poor to good calendering characteristics were observed with
the above batches. The increased molecular weight of
Vistanex B-100 reduced the calenderability of the 50-50
blend. Small samples of the optimum blends calendered on
fabrics showed the same combination of properties as the
press-molded films, i.e., good acid-resistance and excellent
flexibility. Polyethylene-Vistanex blends calendered on
Vinyon formed successful barriers for fuming nitric acid, with
films of thicknesses of seven mils, or more, on seven mils
of fabric.

Because of the nerve of batches containing large proportions
of Vistanex B-80, the coatings were applied to the fabrics
under high stress. When the coating left the calender, it
relaxed causing excessive puckering of the base fabric.
In the processing of nervy batches, solution-coating has a
distinct advantage over calendering. However, since solution-
cast films did not give consistently good acid-resistance,

methods of improving calendering techniques had to be developed. Methods for handling synthetic fabrics also had to be evolved. For example, Dynel fabric was found to distort at the upper calendering temperatures.

The difficulties encountered are apparently quite general throughout the fabric-coating industry. It was believed that the addition of lower molecular weight polyethylene, of the paper-coating type, might ameliorate the nerve of given batches. However, work in this direction revealed that Alathon VII reduced the acid-resistance of polyethylene-Vistanex blends. Pigments improved processing characteristics but also reduced acid-resistance.

Continuous calender-coating of polyethylene-Vistanex blends must be carried out with proper control of calender-roll temperature and speed and the proper preheating of the composition on the mill. The calender-roll temperatures required are largely dependent on the nerve of the batch to be calendered. Higher temperatures are required to calender batches containing increasing proportions of Vistanex B-80, and batches containing even relatively small proportions of Vistanex B-100 cannot be calendered at all.

Since it was thought that plastic flow might be a measure of the ease of calenderability of various polyethylene-Vistanex blends, a series of plasticity number determinations was made. It was found, however, that no high degree of correlation seemed to exist between flow characteristics and ease of processing.

In an evaluation of the performance of various blends on a pilot-plant calender, it was found that stearic acid acted as a plasticizing aid, in that it lessened retraction of the blend and provided better release from the calender rolls. No appreciable change in resistance to nitric acid was noted in blends containing up to five percent stearic acid.

b. Adhesion to Fabric

One of the problems in the calendering of coatings on cloth is that of obtaining adequate adhesion. In an effort to improve the adhesion of polyethylene-Vistanex blends to fabrics, it was found that marked improvement was obtained by priming Vinyon fabric with a solution (10% solids) of Vistanex B-80 dispersed in toluol. The flexibility of the fabric was maintained with very little loss after calendering. Contrary to expectation, methylene bis (4 phenyl isocyanate)

had an adverse effect on adhesion, and imparted boardiness to uncoated fabrics.

Experiments were conducted to determine the adhesion of experimental coatings to various types of primed Dynel and Vinyon fabrics by peel stripping. It was found that the adhesion was greater than the film strength of the coating. All films in thicknesses of eight and twenty-five mils ruptured before any readings could be taken. When a film thickness of fifty-five mils was used, the highest values (4.1 lbs./in. in the direction of the warp and 5.0 lbs./in. in the direction of the fill) were obtained with Vinyon (Flightex Corp.) Style #505 which contains Vinyon fibers in the warp and Dynel fibers in the fill. Values of 2.6 lbs./in. (warp) and 4.7 lbs./in. (fill) were obtained with Vinyon (Flightex Corp.) Style #501 which is 100 percent Vinyon. Intermediate values were obtained with Dynel (U.S. Rubber Co.) Style 902-F and Dynel (U.S. Rubber Co.) Style X-5142.

c. Flame-Resistance

In the coated fabric industry, certain pigments are used to improve flame-resistance. Experiments with polyethylene-Vistanex blends, however, revealed that most pigments decreased the acid-resistance. A number of pigments commonly used as flame-retardants were evaluated but were found to be of no value in the quantities employed.

A study of the use of zinc oxide, bismuth trioxide, Carbon Black P-33, Kel-F Wax #150, Titanox A, antimony trioxide, ammonium chloride, and zinc borate, alone and in combination, revealed that even excessive amounts of these materials would not impart flame-resistance. Flame-retardants were added (Procedure G, Appendix) to previously milled polyethylene-Vistanex blends on a laboratory mill. The flammability of these mixtures was compared with that of previously milled, unfilled polyethylene-Vistanex blends which had been calendered on Dynel. In two cases, blends consisting of 80 parts Vistanex, 20 parts polyethylene and 40 parts titanium dioxide were placed over Vinyon and Dynel fabrics, and the components were subjected to 65 psi at 280°F in a hydraulic press (Procedure G, Appendix). The resultant coated fabrics were brought into contact with a flame, and their degree of flammability was noted. The results of the tests are given in Table 7 in the Appendix.

All blends, filled and unfilled, supported combustion. The flame-resistance of Dynel-backed coated fabrics prepared without

pigments was found to be only fair. Filled blends, calendered
on Dynel and Vinyon backings, did not burn readily when brought
into contact with flame, and showed some tendency to be self-
extinguishing. Some flame-resistance was imparted to the
blends through the use of Dynel and Vinyon as supporting fab-
rics. The use of Dynel and Vinyon is preferable to the usual
flameproofing methods, for the reason that it in no way impairs
the properties of the protective coating.

d. Blocking

The degree of blocking of prepared coated fabrics was deter-
mined in accordance with A.S.T.M. Standard Method D 884-48.
Vinyon and Dynel fabrics, calender-coated with polyethylene-
Vistanex blends containing from 50 to 80 parts Vistanex B-80
and 20 to 50 parts polyethylene, were superimposed (Procedure
H, Appendix) to obtain three possible surface combinations
(coating to coating, coating to backing, and backing to backing).
Each composite was condtioned in a drying oven for 24 hours
at a temperature of 125°F and a pressure of 1.3 psi.

Increased proportions of Vistanex B-80 produced a corresponding
increase in blocking. Samples containing 70 and 80 parts
Vistanex B-80 presented serious blocking problems, although
previous investigation had shown them to be most resistant to
the passage of nitric acid. No blocking was evident in any
of the three surface combinations of fabrics containing 50
and 60 parts Vistanex in the coating. Calendered fabrics
containing no more than 60 percent Vistanex B-80 were free
from blocking and were very flexible. The incorporation of
pigments in polyethylene-Vistanex blends reduced blocking
but likewise reduced resistance to nitric acid.

Although the decrease in blocking characteristics afforded by
the use of polyethylene-Vistanex blends containing 50 and 60
parts Vistanex was offset by an increase in acid-permeability,
sufficient acid-resistance was obtained for the use of such
blends in fabric coatings. The optimum blend was found to be
40 parts polyethylene and 60 parts Vistanex B-80. This blend
has adequate acid-resistance (40 hours), is readily calendered,
possesses excellent flexibility, and presents no blocking
problems. The use of talc is recommended, however, to prevent
any tendency toward blocking.

Selection of Backing Material for Polyethylene-Vistanex Blend

Since all of the coatings except plasticized Kel-F allowed
some acid to penetrate, it was desirable that the fabric,
itself, have some acid-resistance. The selection of the
optimum fabric (Vinyon) was therefore based on degree of
acid-resistance as well as conformance to Specification MIL-
F-4143(USAF). Vinyon not only meets the requirements of
Specification MIL-F-4143(USAF) when used as a base fabric,
but also possesses considerable resistance to nitric acid.
Moreover, Vinyon is flame-resistant and reduces the flammability
of the coated fabric appreciably. Lastly, Vinyon exhibits
better temperature-stability at calendering temperatures than
some of the other thermoplastic fibers.

e. Crease-Resistance

In order to simulate the effect on clothing of folding and
stacking in piles, a crease-resistance test was devised in
which the coated fabric was hung over the edge of a thin
metal sheet, with hundred-gram weights. After the coated
side of the fabric had been in contact with the edge of the
metal for 24 hours at 125°F, the fabric was turned over and
the test was repeated. The creased section was then
subjected to the regular permeability test.

The results which were obtained indicated no reduction in the
resistance of the coated fabric to nitric acid. These find-
ings do not correspond with those reported in the case of the
polyethylene-Vistanex coated fabrics manufactured by the
U. S. Rubber Company for the Quartermaster Corps, in which
the coating was said to have flowed away from the creases,
in storage, and acid-resistance was destroyed. In this
instance, the suits may have been packed in bales. Such
treatment would necessarily lead to extensive wrinkles and
creases in which the coating would be seriously impaired.
Since most of the polyisobutylenes are subject to a certain
amount of cold flow, suits made from fabrics coated with a
polyethylene-Vistanex blend should be handled as garments and
packed with some care. It would be advisable to dust the
suits with talc before storage.

f. Resistance to Oxidizing Agents and Fuels

The general resistance of the coated fabric to the action of
various oxidizing agents and fuels which might be used in
guided missiles, was determined. Samples of the coated fabric
were placed in beakers containing mixed acids (15% fuming
sulfuric and 85% red fuming nitric), hydrogen peroxide (90%),
furfuryl alcohol, aniline and furfuryl alcohol (70%-30%),

ethyl alcohol (commercial), aniline, monoethylaniline, and
ammonia (commercial). The results which were obtained were
favorable. In all cases, no evidence of decomposition of
coating was noted after a 160-hour exposure.

It should be pointed out that in the testing of samples of
the coated fabric by immersion, the fabric is exposed to the
chemicals as well as the coating. Fabric decomposition was
first noted after six hours' exposure to aniline as well as
mixed acids (15% concentrated sulfuric acid and 85% red fuming
nitric acid). Fabric failure occurred after 48 hours' expo-
sure to a mixture of 70% aniline and 30% furfuryl alcohol.

g. Processing of a Colored Fabric

Wright Field had expressed a desire for a white suit to be
used in tropical areas, and a green suit to be used in cooler
regions. It was found that a satisfactory white color could
be obtained by the use of those pigments which have high
tinting strength, such as titanium dioxide, in small enough
quantities to avoid undue reduction in acid-resistance (5 parts
per 100 parts of blend).

In developing a green, coated fabric, an investigation was
carried out to determine the effect of using an unpigmented
polyethylene-Vistanex blend over a fabric which had been
dyed green. An unpigmented blend of 60 parts Vistanex B-80,
40 parts polyethylene (Alathon A) and 2 parts stearic acid
on Vinyon Fabric #505 (blue-green) resulted in a finished
fabric having a uniform blue-green color. It is believed
that a coated fabric can be produced in any color desired,
by the use of the polyethylene-Vistanex blend on a properly
dyed base fabric.

4. Production Calendering of Blend on Fabric

At the time when samples of polyethylene-Vistanex blends
produced on a pilot-plant calender on primed Vinyon Fabric
#501 were found to meet the requirements of a coated fabric
for use in protective clothing, arrangements were made with
the Hodgman Rubber Company in Framingham, F   chusetts, for
the production-calendering of 240 yards of   yon fabric.
Several visits were made there to select the optimum compo-
sition for calendering in production quantities. In a
study of the performance of blends on the calender, Hodgman
Rubber suggested that stearic acid be used as a processing
aid to reduce the nerve of the stock. Laboratory investigation

subsequently revealed that stearic acid could be used in
quantities up to five percent without any appreciable effect
on the resistance of the fabric to nitric acid.

A final selection of the optimum polyethylene-Vistanex blend
for a production run was made on the basis of calenderability,
acid-resistance and lack of blocking. It was decided that a
mixture of 60 parts Vistanex B-80, 40 parts polyethylene,
5 parts titanium dioxide and 2 parts stearic acid would be
used. A master batch of the mixture was prepared and sent,
together with the Vinyon and sufficient Vistanex B-80
solution (18% solids in toluene) as primer, to the Hodgman
Rubber Company.

On June 25, 1953, the two hundred and forty yards of Vinyon
Fabric #501 were successfully calendered on production
equipment. No production difficulties were encountered in
either the priming or the calendering operation. The fabric
was processed on a four-roll, Farrel-Birmingham calender, at
the rate of 20 to 25 yards per minute. Calendering conditions
were as follows:

Temperature of the Rolls	Top Roll, 260°F
	Second Roll, 275°F
	Third Roll, 270°F
	Bottom Roll, 190°F
Weight of Primer	1.0 - 1.25 ounces per square yard
Weight of Polyethylene-Vistanex Coating	5-6 ounces per square yard

The polyethylene-Vistanex coating was deposited smoothly
across the base fabric, and was of uniform thickness. When
the finished fabric was subjected to the DuPont Scrub Test,
it withstood 200 cycles, indicating that the coating was
not only well adhered but possessed excellent strength.

Inspection of Coated Fabric

Unfortunately, a few pinholes were evident in the coating.
Some of these had apparently been caused by contamination
from small metallic particles which had been picked up in
the milling operation. Tests were run on samples of the
coated fabric both before and after repair of the pinholes,

to determine the degree of resistance to nitric acid. It was found that samples containing minute pinholes which had not been repaired withstood exposure to nitric acid for a period of about 10 hours before permeation of 2.5 grams per square meter occurred. Samples containing pinholes which had been repaired withstood exposure for a period of 30 hours before 2.5 grams of nitric acid penetrated through the fabric, which is nearly equivalent to the perfect material.

In repairing the pinholes, the coated fabric was inspected by passing it over a wire frame with electric lights underneath, which provided effective means for visual inspection (Figure 12). A drop of calendered polyethylene-Vistanex blend dispersed in xylene was placed over each pinhole and was allowed to air-dry. The treated surface was then heat-sealed by means of a soldering iron, placed in contact with a piece of Teflon which was laid directly over the pinhole.

When the pinholes had been repaired, a sufficient quantity of the coated fabric was shipped to the manufacturing plant of S. Froelich & Sons in New London, Connecticut, with whom arrangements had been made for the fabrication of protective suits.

5. Fabrication of Protective Clothing

The experience of manufacturers who have made articles of coated protective clothing or foul-weather gear which must pass a hydrostatic test has been that the greatest difficulty encountered is that of obtaining tight seams. Recognizing this problem, The Connecticut Hard Rubber Company's first approach to the matter of fabricating clothing was an evaluation of methods of protecting the seams. This is usually accomplished by means of solvent solution coatings which are economical and easy to apply. However, solvent solution coatings were not desirable for use in this case, since polyethylene-Vistanex solutions can only be used hot (160°F) and the garment must be held at 160°F in order to obtain crack-free films.

A visit was paid to Mr. F. Duske of Brooks Brothers. Mr. Duske had formerly been associated with the International Tailoring Company which had made a great many raincoats and foul-weather gear for the Navy. He described the problems which had to be overcome in order to obtain seams in the garments which would pass the hydrostatic test. Mr. Duske suggested that the seams of the acid-resistant, protective suits be taped and also be heat-sealed by means
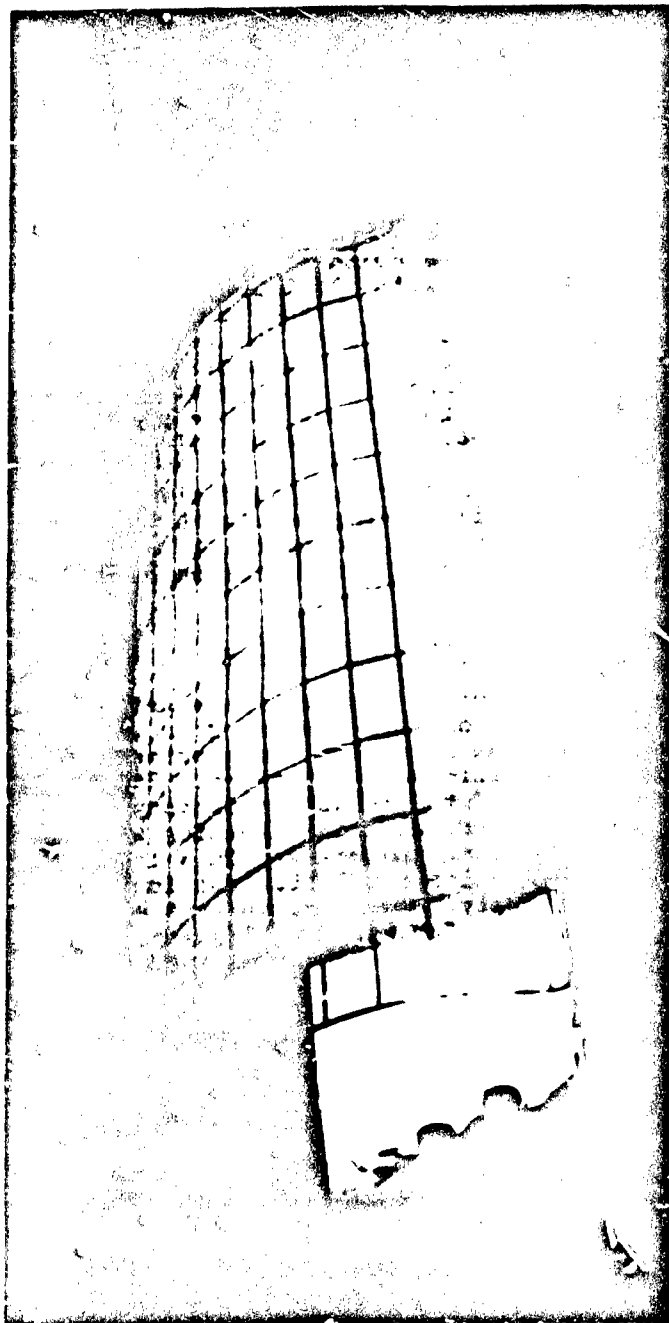
FIG.12- INSPECTION TABLE FOR COATED FABRIC.

of an electrically heated roller with a recessed area in the
center so that no pressure would be applied to the seam,
itself, during the sealing operation. Otherwise, some of
the adhesive would be squeezed out from under the tape.
Moreover, the heat might damage the stitching. In accor-
dance with his suggestions, a number of tests were run on
the peel-strength of taped seams. Both unsupported polyethy-
lene-Vistanex film and two-side coated fabric were evaluated
as the tape material. Both were found to be equally satisfac-
tory.

a. Protection of Seams

When the actual fabrication of articles of protective cloth-
ing, such as sleeves and gloves, was initiated in the
laboratory, special consideration was given to the problem of
maintaining the nitric acid barrier at the seams. The
initial laboratory work was concerned with an evaluation of
methods and materials for protecting seams which had been
sewn by hand with Vinyon thread. In the meantime, arrange-
ments had been made with a local seamstress for the fabrica-
tion of a prototype sleeve, sewn with Vinyon thread. Arrange-
ments had also been made with S. Froelich & Sons, New York,
N. Y., for the fabrication of protective suits and hoods,
conforming to patterns designed by the Quartermaster Corps.

Experimental work revealed that the seals obtained by coating
with solvent solutions of Vistanex B-80 or the polyethylene-
Vistanex mixture were inferior to taped seams, which was to
be expected in view of the fact that the acid-resistance of
solvent solution coatings is relatively poor. However, it
was discovered that the technique of applying and fusing
multiple coats of a hot solvent solution of polyethylene-
Vistanex effectively reduces the amount of residual solvent
and thereby increases the degree of acid-resistance.

Taped seams obtained by the use of solvent solutions of either
Vistanex or the pigmented polyethylene-Vistanex blend as
adhesives, and either unsupported polyethylene-Vistanex tape
or two-side coated fabric as reinforcing tapes were evaluated
by means of peel-strength tests. While both adhesives were
equally satisfactory, the use of the solvent solution of
Vistanex is definitely more practical, since the solvent
solution of the polyethylene-Vistanex blend has to be main-
tained at a temperature not less than 160 °F for application,
or "mud-cracking" will occur. The two-side coated fabric
appeared to be the more satisfactory seam binding from the
standpoint of providing greater mechanical strength. However,

the unsupported tape composed of the polyethylene-Vistanex mixture was more than adequate for sealing purposes, and was more flexible than the tape made from the coated fabric.

The optimum procedure for protecting seams was found to consist in coating the seams with Vistanex in solvent (18% solids in xylene) in a width of 1-3/4 inches over the seam area, allowing it to air-dry for about fifteen minutes, and heat-sealing with an unsupported tape of the pigmented polyethylene-Vistanex blend. Sealing was accomplished by means of an electrically heated roller designed with a recess in the center so that no pressure is applied on the seam itself. The section of the garment undergoing heat-sealing must be held under moderate tension while the operation is in process. In the case of the sleeve, a piece of plywood was cut to a shape to conform to the sleeve, and the sleeve was placed on the form in such a way that the seam was in the center of the plywood.

b. Suits and Hoods

Four protective suits and two hoods were successfully fabricated by S. Froelich & Sons from the previously prepared coated fabric. Two of the suits were made with cuffs on the sleeves, and two without. Lock-stitch Singer sewing machines were used. Stitching was done with Dacron thread because of the ease with which it is handled on the sewing machines and because of its great toughness. The thread was treated with paraffin wax before use to prevent the needles from sticking. The sewing characteristics of the coated fabric are considered good. The suits weigh approximately two pounds, each, and possess a flexibility approaching that of normal wearing apparel.

Sealing of the seams of the suits was carried out at The Connecticut Hard Rubber Company. Two of the suits were sealed by the use of tape, coated on both sides with the polyethylene-Vistanex blend, in the manner described under "Protection of Seams". It was the opinion of Wright Field that the seams of these suits were too stiff, and they requested that attempts be made to attain more flexibility of the seams by the use of other means for sealing. Therefore, the other two suits were sealed with the unsupported polyethylene-Vistanex tape. Plywood forms were used for all sections of the suits, to provide a flat surface at the seam areas during the heat-sealing operation and to keep the areas

under moderate tension.

The hoods were sealed at the seams in the same manner as was used with the suits. A piece of polyvinyl plastic (manufactured by B. F. Goodrich Company) of the standard Quartermaster Corps design, was used as a face shield in each of the hoods. The front, side and rear views of the protective clothing can be seen in Figures 13, 14, and 15.

c. Gloves

There were two possible approaches to the fabrication of acidproof gloves. One was to make a dip-coated glove. The other was to make a glove from the calendered polyethylene-Vistanex fabric, which offers the greatest amount of acid-resistance, and to tape the seams to provide protection. However, because of the complexity of the construction of a glove, it was not feasible to tape the seams. The initial laboratory work on the development of acidproof gloves was therefore concerned with an investigation of the potentialities of dip-coating.

As noted earlier, it was necessary to maintain the solvent solution of the polyethylene-Vistanex blend at a temperature of 160°F to prevent mud-cracking. A study was made of solvents having boiling points above the fusion temperature of the polyethylene-Vistanex blend. A mixture of cumene and xylene (about 1 to 4) proved to be more practical for use as the high-boiling solvent than cumene, itself, which was difficult to remove from the film. Solution-cast films of the pigmented polyethylene-Vistanex blend were prepared for acid-resistance tests. A film (.020 in. thick) cast from the mixture withstood exposure to nitric acid for 28 hours before penetration of 2.5 grams per square meter. Further work with hot solvent solutions of the polyethylene-Vistanex blend led to increased acid-resistance.

Work done at this time on the preparation of a solution-cast film of Vistanex B-80 in toluol indicated good acid-resistance only in thicknesses too great for practical use. Gloves cut from plain Vinyon, and sewed with Vinyon thread, were coated by dipping in Vistanex, and were sealed at the seams by the use of the polyethylene-Vistanex blend. Here, too, it was found that Vistanex coatings provided acid-resistance only with a multiplicity of dippings.

FIG.13- PROTECTIVE CLOTHING. FRONT VIEW.
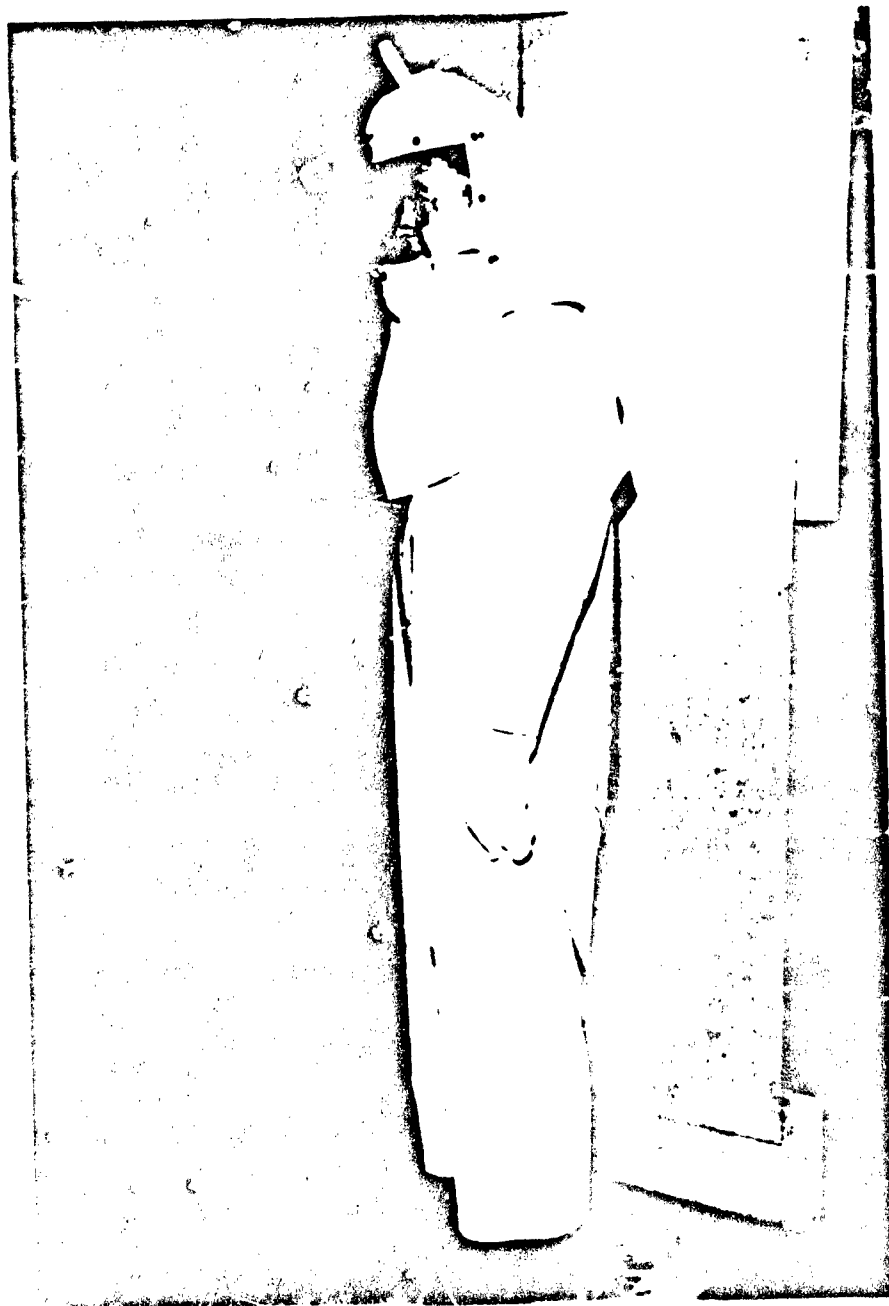
FIG 14 - PROTECTIVE CLOTHING SIDE VIEW
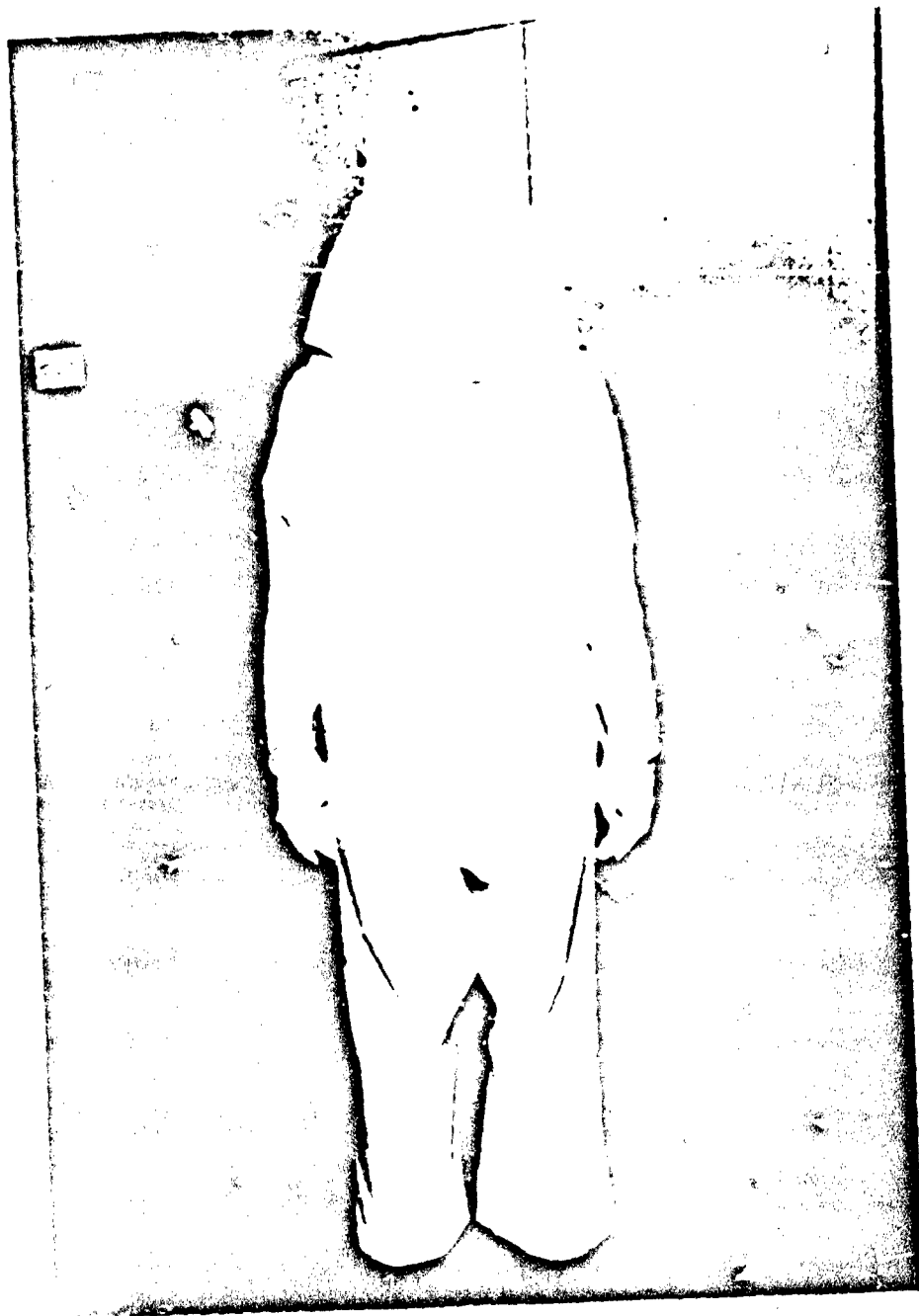
FIG. 15 - PROTECTIVE CLOTHING, REAR VIEW

It was found that it was not practical to coat gloves with the use of standard dip-coating techniques, since the coating penetrates too deeply into the fabric. However, techniques for applying the pigmented polyethylene-Vistanex blend to uncoated cotton gloves without the formation of cracks were developed. A continuous surface could be obtained by the proper control of temperatures during the dipping and drying operations. The glove was immersed in the solvent solution which had been heated to 160°F. After removal from the bath, the glove was immediately placed in a drying oven for a period of 15 minutes, while a temperature of 160°F was maintained. This process was repeated until the desired thickness (about .012 in.) was obtained. Gloves prepared in this manner, however, were still relatively inflexible (Figure 16, Glove 1). Rubber gloves coated in this manner (Figure 16, Glove 2) exhibited optimum flexibility. While the adhesion of the coating was considered good, improvements were noted with the use of a primer coat of Vistanex in xylene.

Arrangements were made with S. Froelich & Sons for the fabrication of some gloves from the calendered fabric. The principal difficulty encountered in sewing the gloves was that the fabric slipped in the sewing machine. The tension exerted on the fabric during the sewing operation was not even. Bunching between the fingers resulted (Figure 16, Glove 3). and the gloves were difficult to seal. This indicated that a better method of fabricating the gloves should be developed.

A visit was paid to the Edmont Manufacturing Company, Coshocton, Ohio, who are the largest manufacturers of coated gloves in the industry. The problem of preparing a satisfactory acidproof glove was discussed with them at length. A number of pairs of gloves were cut from the coated fabric, and sewed with cotton thread. It was discovered that it was somewhat more difficult to sew the coated fabric on a chain-stitch machine than on a lock-stitch machine. The polyethylene-Vistanex mixture stuck to the needles, and caused the machine to skip. This difficulty was eliminated by dipping the thread into paraffin wax, and by holding a little artist's brush, which had been dipped in wax, against the needle. The gloves were sewn on chain-stitch machines, manufactured by the Union Special Machine Company. The machines had a guide near the presser foot to keep the distance between the edge of the fabric and the seam at a constant predetermined value.
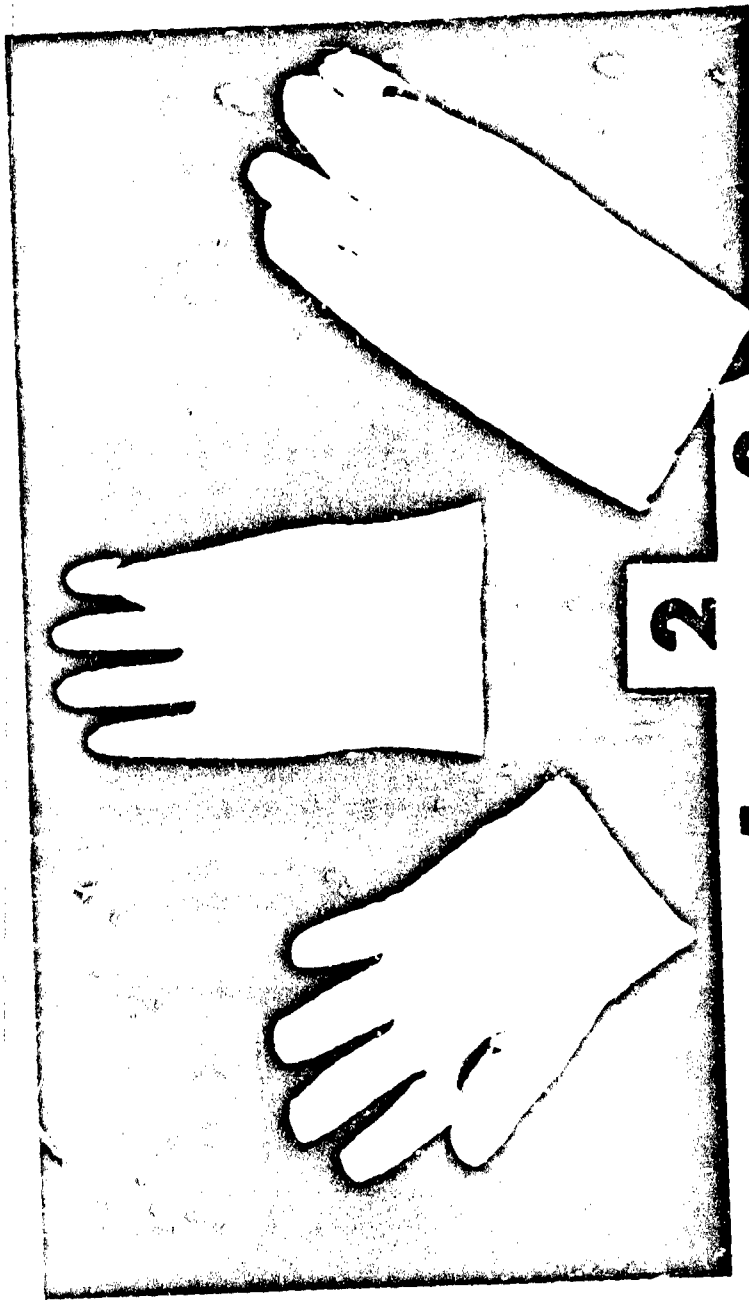
FIG. 16 — VARIOUS TYPES OF POLYETHYLENE-VISTANEX COATED GLOVES.

After the gloves were sewn, they were mounted on forms. It
is very important that the glove should fit the form, since
wrinkles cause imperfections in the coating. It is therefore
necessary that the fabric have a certain degree of stretch.
When the gloves are cut from the fabric on the square, there
is absolutely no stretch. However, a later experiment showed
that the fabric can be made to exhibit considerable stretch
if it is cut on the bias. Although no gloves made by this
method were dipped, enough work was done to demonstrate that
bias-cutting would provide sufficient stretch to allow the
gloves to fit the form and thus render them sealable by
dipping.

The solvent solution of polyethylene-Vistanex blend was
heated to 160°F. The gloves, mounted on the forms which had
been preheated to prevent any chilling of the solution, were
dipped, fingers down, into the solution. The gloves were
then transferred immediately to an oven maintained at a tem-
perature of 180°F, where they were allowed to dry for ten to
fifteen minutes. The process was repeated until the desired
number of coats had been applied. The seams of gloves made
from the calendered fabric were effectively sealed by this
dip-coating process.

Some neoprene-coated, woven fabric gloves were used in dipping
experiments to determine whether the polyethylene-Vistanex
mixture would adhere satisfactorily. The results were good, and
the coating could be peeled off the neoprene only with diffi-
culty. It was believed that even this adhesion might be
improved by the use of a base coat of straight Vistanex as
a binder.

Arrangements were made for the Edmont Manufacturing Company
to supply The Connecticut Hard Rubber Company with knit-cuff,
neoprene-coated, cotton flannel work gloves, some having only
a light coating of neoprene to prevent the polyethylene-Vistanex,
subsequently applied, from flowing into the fabric, and some
carrying a standard neoprene coating (.020 in.). The gloves
having the light coating of neoprene were dip-coated in a
hot solvent solution of the polyethylene-Vistanex blend at
The Connecticut Hard Rubber Company. While the adhesion
of the coating to the neoprene was not as good as it might
have been if Vistanex had been used as a primer, the gloves
looked quite promising.

One pair of these gloves and two pairs of white gauntlets con-
sisting of the same material used in the suits and hoods, which
had been multiple dip-coated in hot solvent solutions of the
polyethylene-Vistanex blend to provide protection for the seams,
were shipped to the Wright Air Development Center.

C. Teflon and Kel-F Films

In the early step of work on this pro' ot, Teflon and Kel-F were thought to be the most promising materials for the development of fabrics whith would be resistant and impermeable to oxidizing agents and fuels used in guided missiles. These materials possess excellent chemical resistance and some flexibility, a characteristic necessary in protective clothing. The chemical, physical and mechanical properties of Teflon and Kel-F are discussed in the Literature Survey, 2. Properties of the Fluorocarbon Polymers.

Since white fuming nitric acid is one of the more severe materials of those specified for use in the testing of the fabric, it was felt that impermeability to this acid would be the best criterion of its resistance to chemicals.

As a preliminary step in the evaluation of these materials, a number of permeability tests were run on commercial films and films cast from commercial dispersions.

In the case of extruded Kel-F films, the resistance to acid-penetration was extremely good. In one case, a thickness of only two mils was resistant for over 400 hours (Figure 17). A second sample was considerably inferior. It was therefore concluded that a thickness of two mils is somewhat below the minimum thickness for safety against penetration of nitric acid, whereas seven mils is perfectly safe. Films cast from highly plasticized Kel-F dispersions also showed a high degree of impermeability, as will be seen later. Specimens of Teflon film made both by extrusion and by shaving from a block showed relatively poor acid-resistance (Figure 18).

Teflon is extremely resistant to attack by chemicals, but the permeability tests indicated a microporous structure. In an attempt to plug these holes, a number of commercial and cast films were treated with low molecular weight halocarbon greases and waxes.

Commercial Teflon films, .003 in. thick, were placed in hot melts of Kel-F waxes #40 and #150 and Halocarbon Wax 10-00 and treated at 300°F for one hour. Removal of the films from the hot melts of the #150 and #40 waxes resulted in the immediate solidification of the waxes, making it necessary to wash the films before testing. In the case of the #10-00, the brittle deposit of the wax could be peeled off, showing lack of interaction at this temperature.

Test results on these films showed only a slight improvement (Figure 19), so two other sets of commercial Teflon films,
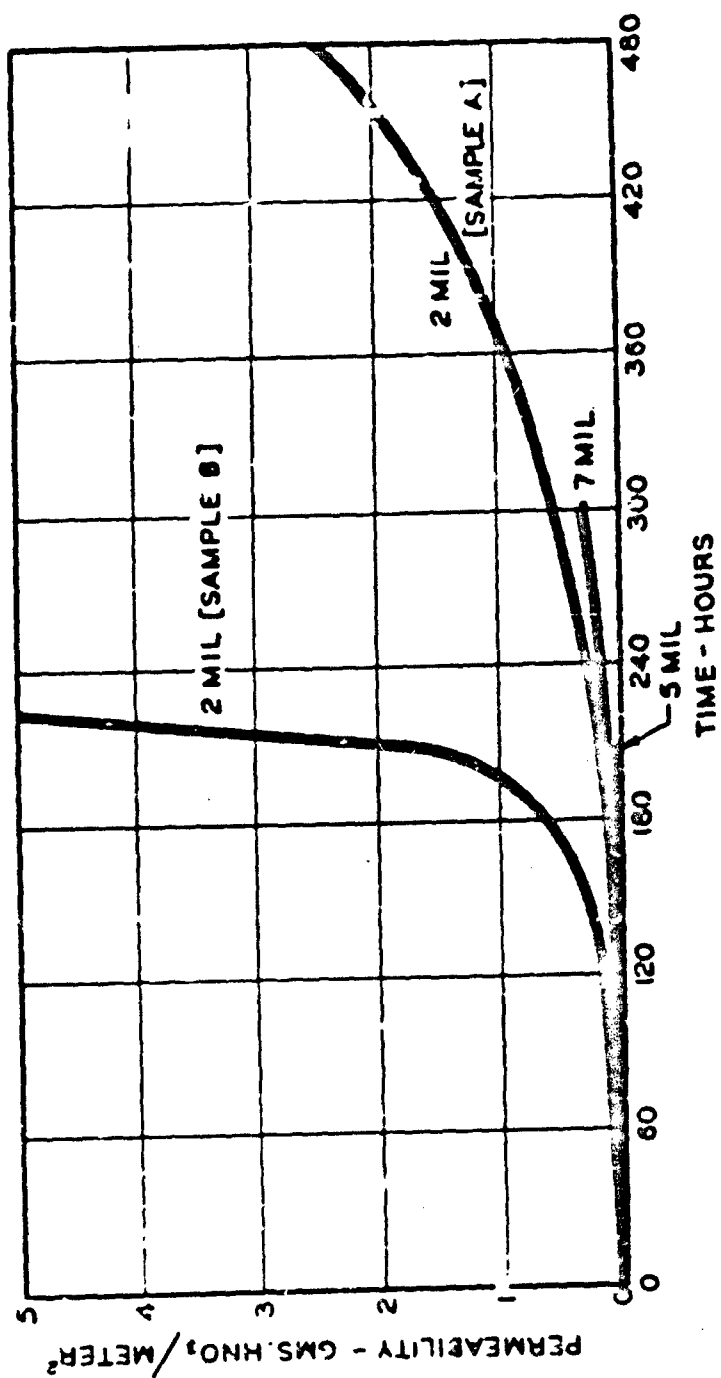
FIG.17-NITRIC ACID PERMEABILITY OF COMMERCIAL EXTRUDED KEL-F FILM.
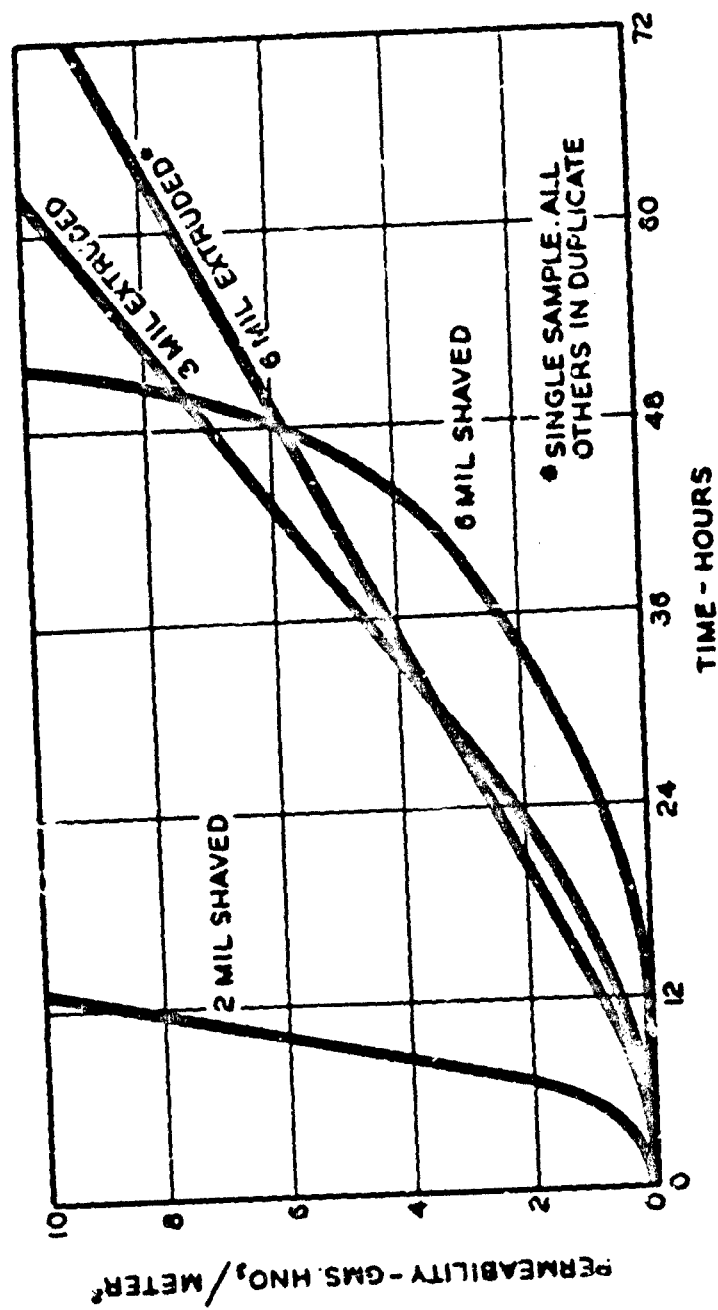
FIG.18-NITRIC ACID PERMEABILITY OF COMMERCIAL TEFLON FILMS.
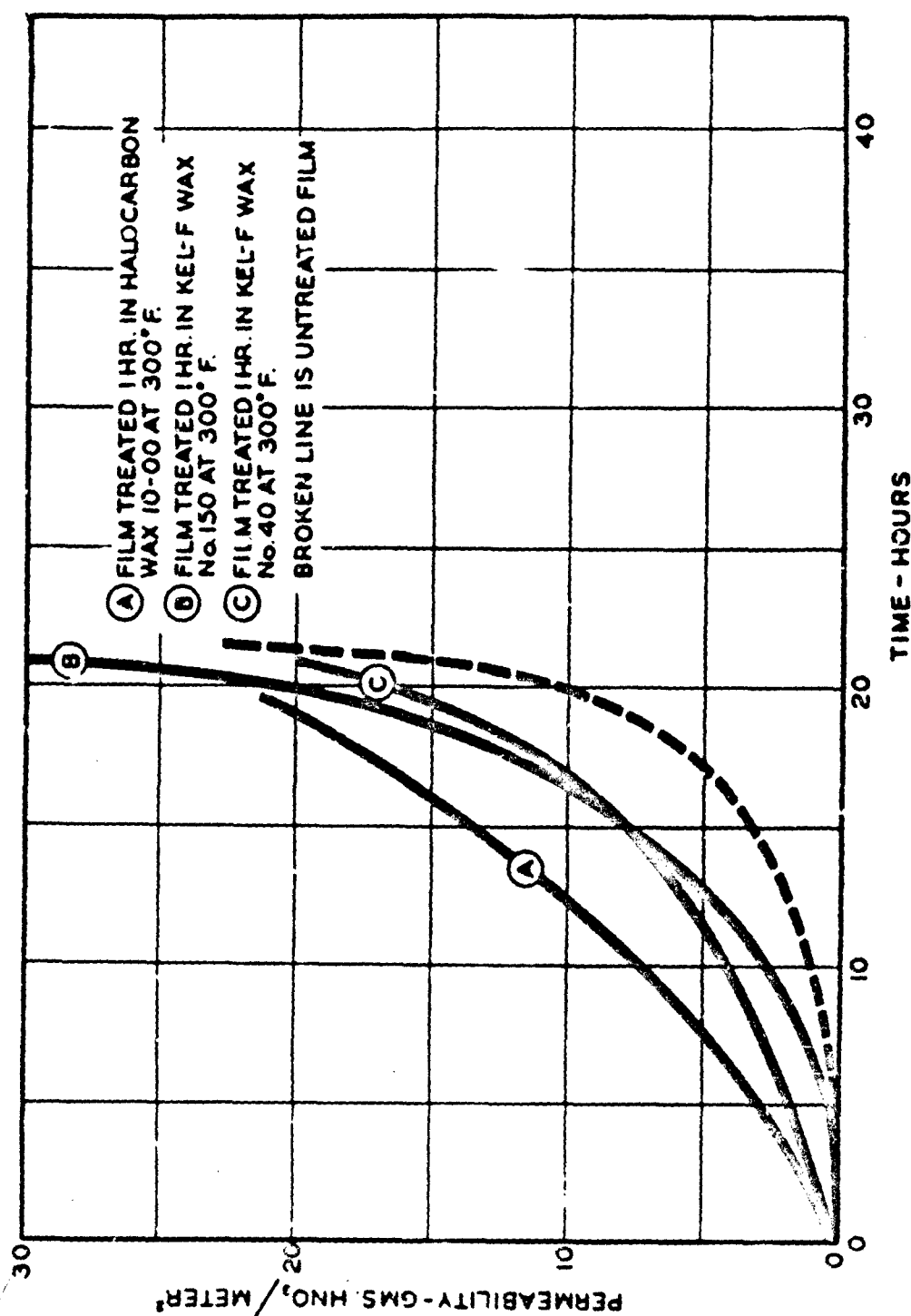
FIG.19-NITRIC ACID PERMEABILITY OF IMPREGNATED
TEFLON FILMS [003"]

(A) FILM TREATED I HR. IN HALOCARBON
WAX 10-00 AT 300°F.
(B) FILM TREATED I HR. IN KEL-F WAX
No.150 AT 300°F.
(C) FILM TREATED I HR. IN KEL-F WAX
No.40 AT 300°F.
BROKEN LINE IS UNTREATED FILM

.006 in. thick, were treated, as above, but at temperatures of 400°F and 480°F for one and two hours. The films were washed with toluene and tested. As shown in Figures 20 and 21, there is no significant improvement in the acid impermeability of films impregnated in this manner.

Attempts were then made to form Teflon films from commercial dispersions. An aqueous dispersion of Teflon was brushed onto clean stainless steel plates. The plates were placed in an oven at 100°C to evaporate the water and then placed in an oven at 720°F for five to ten minutes fusion. The plates were removed and quenched in running water. Additional coats were applied until the desired thickness was obtained. Permeability test results (Figure 22) were poor, showing these Teflon films to be porous.

Steps were taken to repair the microvoids in the film. A film of Teflon was prepared, as above, by fusing successive deposits of particles from dispersion at 720°F. Halocarbon wax (#10-00) was then melted and brushed on the surface of the Teflon film, and the whole was fused at 720°F for five minutes. On removal from the oven, the film was quenched and tested for acid-permeability. The results showed a slight improvement over the plain Teflon film (Figure 22). Other untreated Teflon films, graphed in this figure, show decreasing permeability with increasing thickness. However, in no case was Teflon resistance comparable to Kel-F.

As was mentioned previously, extruded films of Kel-F withstood nitric acid penetration for over 400 hours (Figure 17).

Initial work on cast Kel-F films showed poor acid-resistance due to porosity. In order to make films that would be less porous, several methods were tried, as follows: first, by fusing at higher temperatures, secondly, by plasticizing with lower molecular weight Kel-F polymers in order to lower the fusion temperature, and lastly by plugging the microvoids with materials which would be readily soluble in ordinary solvents.

To study the effect of high-temperature fusing, a heavy deposit of unplasticized Kel-F dispersion was fused on a glass plate for 15 hours at 480°F. The surface was cracked in places and showed some surface irregularities. The film was then placed in an oven at 600°F for three hours. The film showed no improvement in surface characteristics and was slightly more brittle. This film showed poor acid-resistance (Figure 23), and it was therefore concluded that the dispersion method of producing Kel-F films was not feasible without modification.
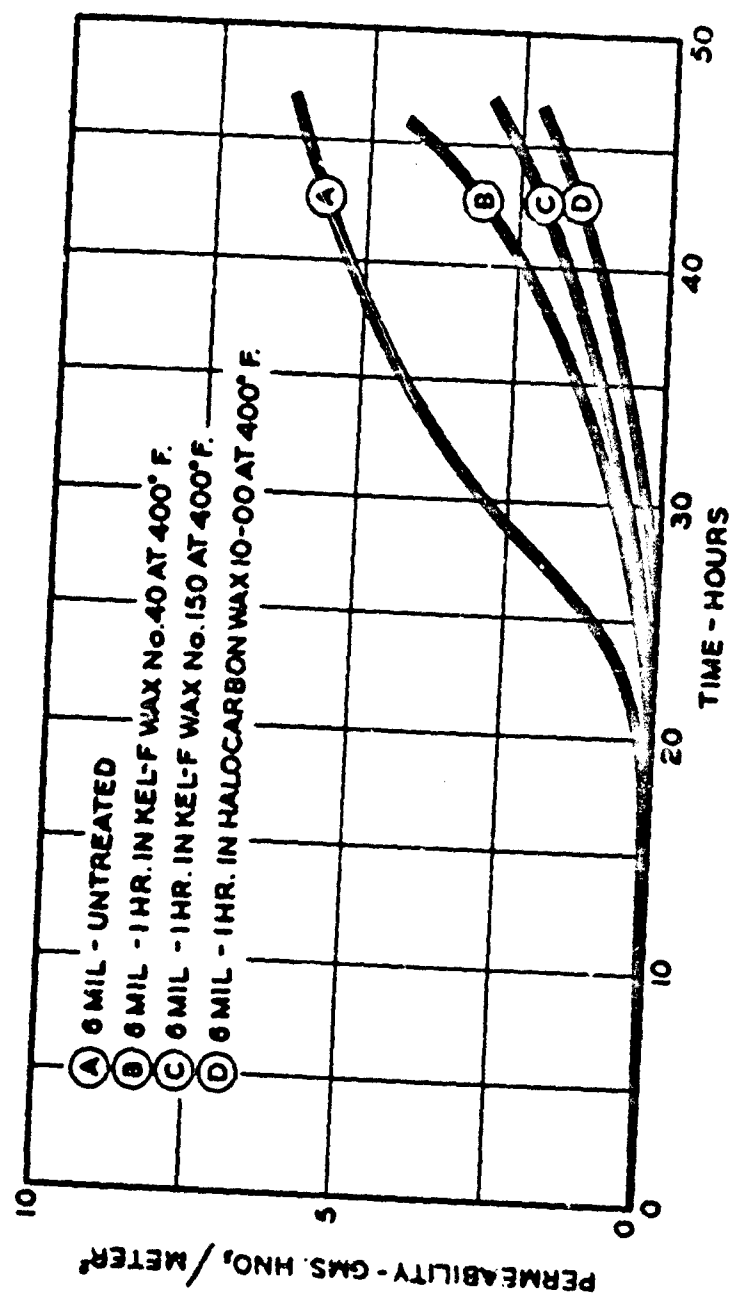
FIG.20-NITRIC ACID PERMEABILITY OF IMPREGNATED TEFLON FILMS [.006"]

Legend:

(A) 6 MIL - UNTREATED
(B) 6 MIL - 1 HR. IN KEL-F WAX No.40 AT 400° F.
(C) 6 MIL - 1 HR. IN KEL-F WAX No.150 AT 400° F.
(D) 6 MIL - 1 HR. IN HALOCARBON WAX 10-00 AT 400° F.

X-axis: TIME - HOURS
Y-axis: PERMEABILITY - GMS. HNO_3 / METER²

FIG. 21- NITRIC ACID PERMEABILITY OF IMPREGNATED TEFLON FILMS [.006"]

A 6 MIL - 2 HRS. IN KEL-F WAX No. 40 AT 480°F.
B 6 MIL - 2 HRS. IN KEL-F WAX No. 150 AT 480°F.
C 6 MIL - 2 HRS. IN HALOCARBON WAX 10-00 AT 480°F.
D 6 MIL - UNTREATED

TIME - HOURS

PERMEABILITY - GMS. HNO₃ / METER²
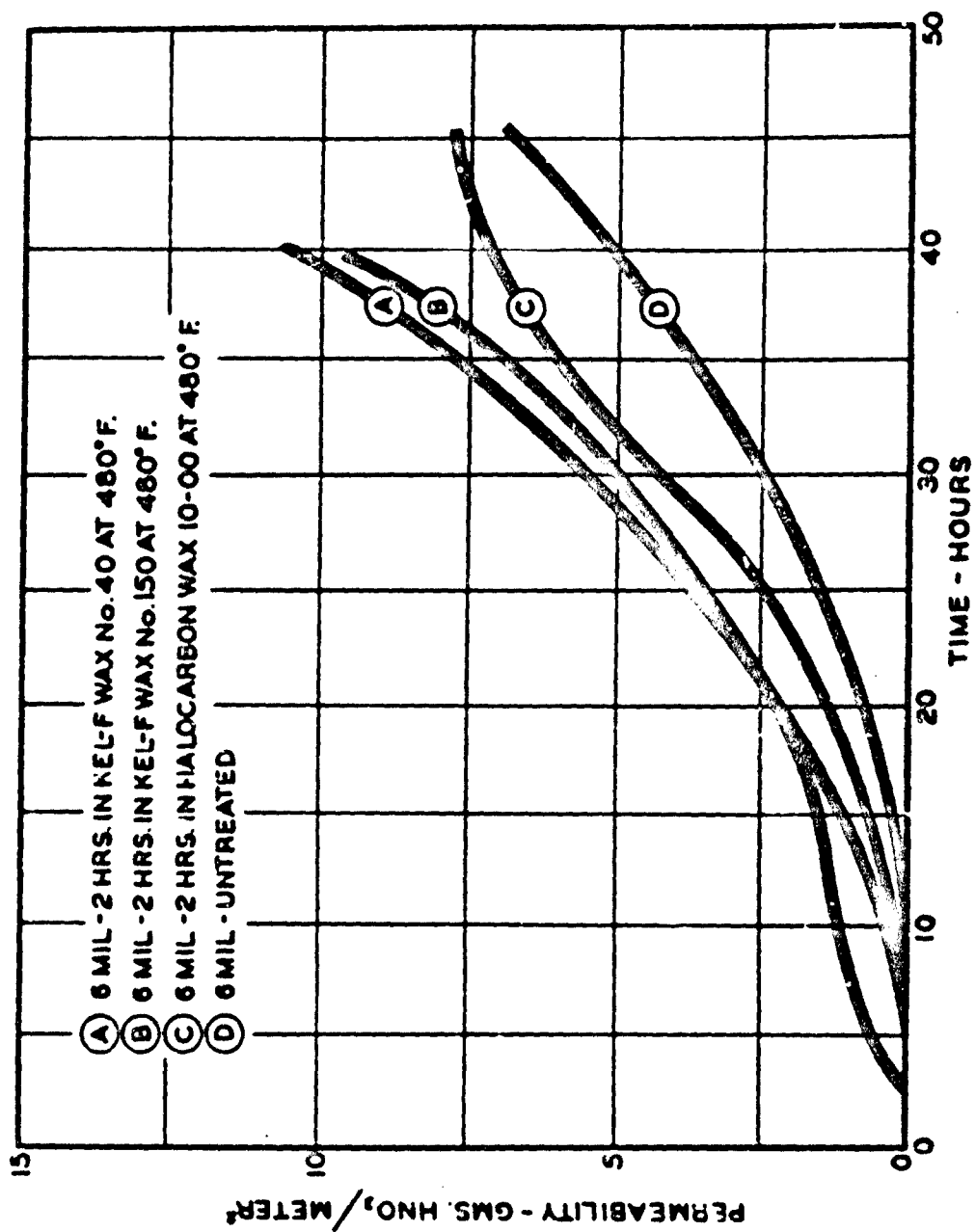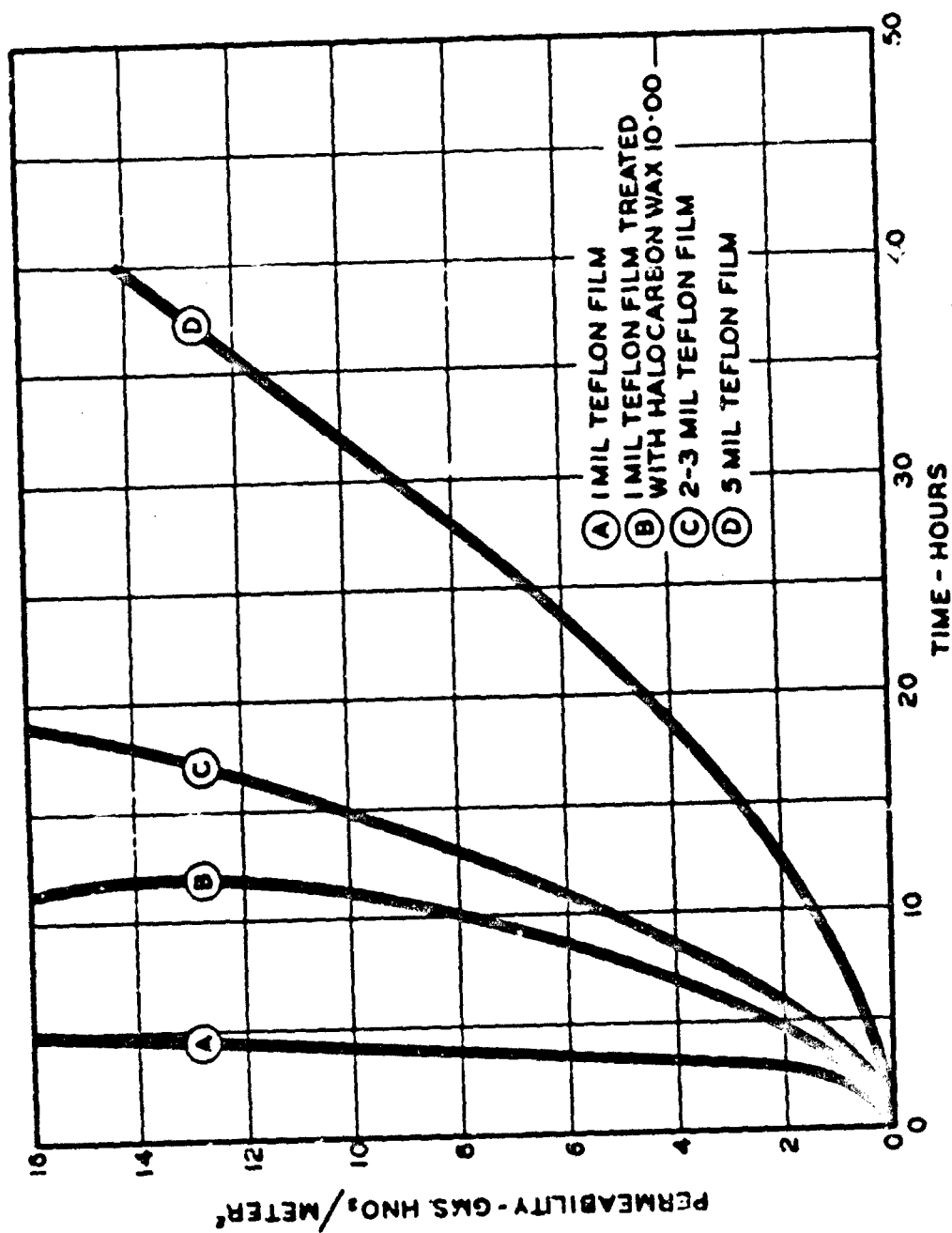
FIG. 22 - NITRIC ACID PERMEABILITY OF DISPERSION -
CAST TEFLON FILMS.

Legend (chart):

(A) 1 MIL TEFLON FILM
(B) 1 MIL TEFLON FILM TREATED WITH HALOCAREON WAX 10·00
(C) 2-3 MIL TEFLON FILM
(D) 5 MIL TEFLON FILM

Axis labels:
PERMEABILITY - GMS HNO₃/METER²
TIME - HOURS

- - - - CAST TEFLON FILMS.
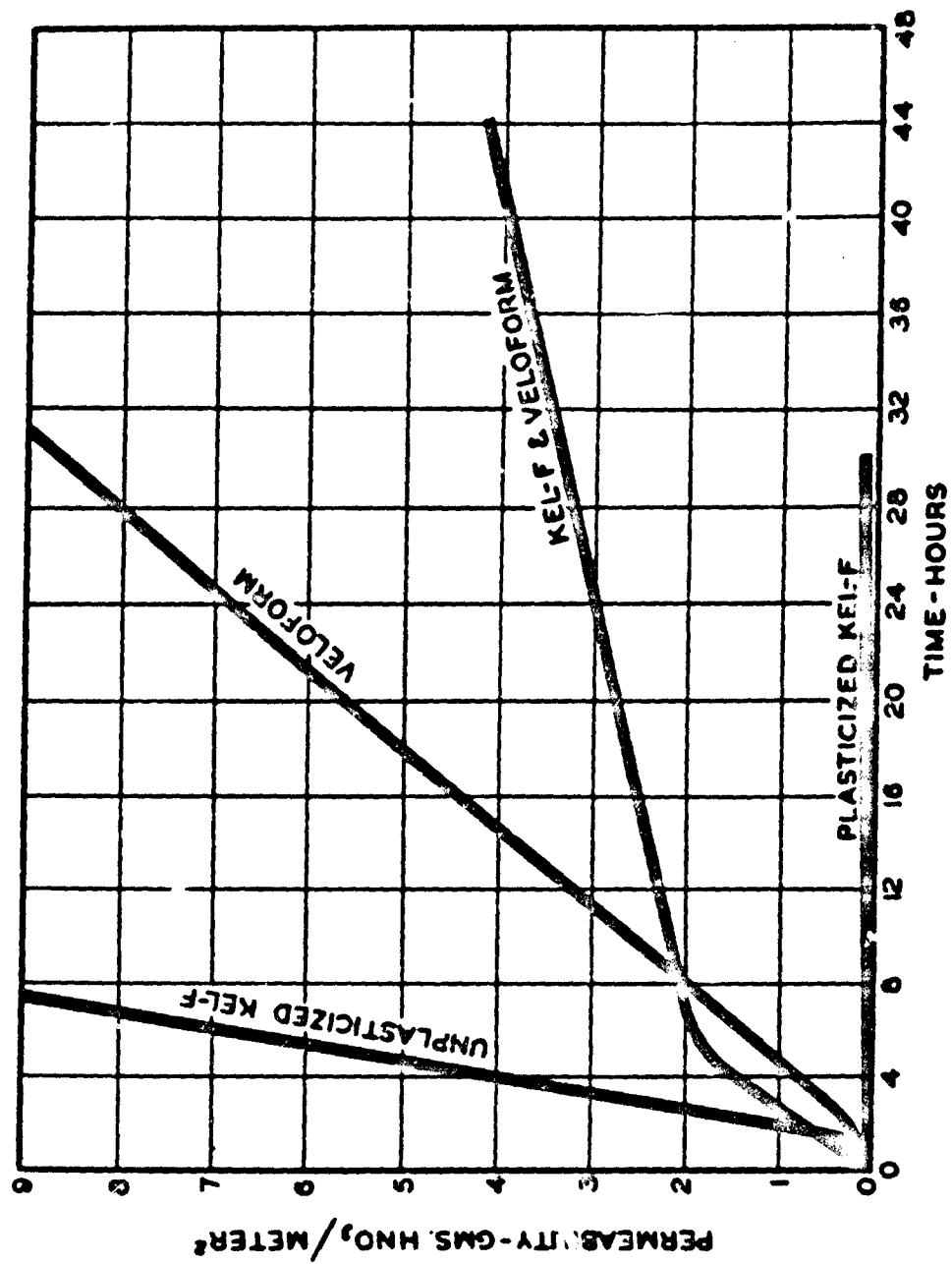
FIG.23-NITRIC ACID PERMEABILITY OF DISPERSION - CAST KEL-F FILMS.

Attempts were then made to cast Kel-F films from highly plasticized dispersions. A low molecular weight polymer (Kel-F #40) was mixed with the dispersion, the amount of #40 being calculated to be 50% of the weight of the solids in the dispersion. The dispersion was diluted with an equal volume of toluene. Films were cast by pouring the resultant mixture onto glass plates, allowing the solvent to evaporate and then fusing at 480°F from 4 to 15 hours.

Films cast with this plasticized dispersion showed great promise. Films obtained through the fusion of one deposit were on the order of .001 in. thick and showed little or no impermeability. By the use of multiple coats, films of .002 to .003 in. were produced which showed a high degree of impermeability (Figure 23).

Veloform, F-10, a copolymer of monochlorotrifluoroethylene and polyvinyl chloride (Procedure K, Appendix) showed moderate resistance to penetration (penetration of 2.5 gms. HNO_3/sq. meter, 10 hrs.).

Since the permeability test on Veloform showed fairly good results (Figure 23), attempts were made to plug the microvoids in the cast Kel-F films with this material in the following manner. An unplasticized Kel-F dispersion was poured on a plate, and the solvent was allowed to evaporate. The resultant deposit was fused at 480°F for 15 hours, and a film approximately .007 in. thick was obtained. This film was coated with the Veloform solution and allowed to air-dry for 24 hours. Permeability tests were then run. There was a marked improvement over both the Veloform film and the cast unplasticized Kel-F film (Figure 23).

In all cases the extruded Kel-F film was the best, being resistant for over 400 hours, while the plasticized Kel-F film was next in line being resistant for over 60 hours (Figure 23).

Permeability data obtained with cast films revealed that various materials showed wide differences in behavior. Polyvinyl chloride, which has been used in fabricating the protective clothing in present use, was found (Procedure I, Appendix) to possess very poor resistance to penetration by fuming nitric acid, even when unplasticized (penetration of 2.5 gms. HNO_3/sq. meter, .5hr.). At first, it was suspected that the solvent might be causing the rapid permeation, but efforts to increase the impermeability of polyvinyl chloride films by heat-treatment (Procedure J, Appendix) were unsuccessful.

Figure 24 shows the rate of penetration of nitric acid into various polyvinyl chloride materials. Curve A represents some olive-drab suit material obtained from Wright Field. Curve B is the white suit material being used in some of the Quartermaster Corps' suits. Neither of these fabrics has satisfactory resistance to nitric acid. Curves C, D and E represent solution-cast films of unplasticized polyvinyl chloride, air-dried and oven-dried. The data upon which these curves are based may be found in the Appendix, Table 6,1 through v.

Figure 25 is a graphic comparison of the resistance of polyvinyl chloride, both as coated fabric and unplasticized film, and the resistance of a solution-cast film obtained from a mixture of 30 percent Vistanex and 70 percent polyethylene. The data upon which these curves are based may be found in the Appendix, Tables 1, i, 6, iv and 6, vi.

The ability of Vistanex, a material which has poor resistance to nitric acid, to overcome the porosity of polyethylene led to the investigation of another material as a possible additive to polyethylene. Steps were taken to prepare blends of Veloform and polyethylene in the same range of concentration as Vistanex-polyethylene blends. However, so many difficulties were encountered in obtaining homogeneous solutions or dispersions and in the casting of the films that further investigation of this combination of materials was abandoned.
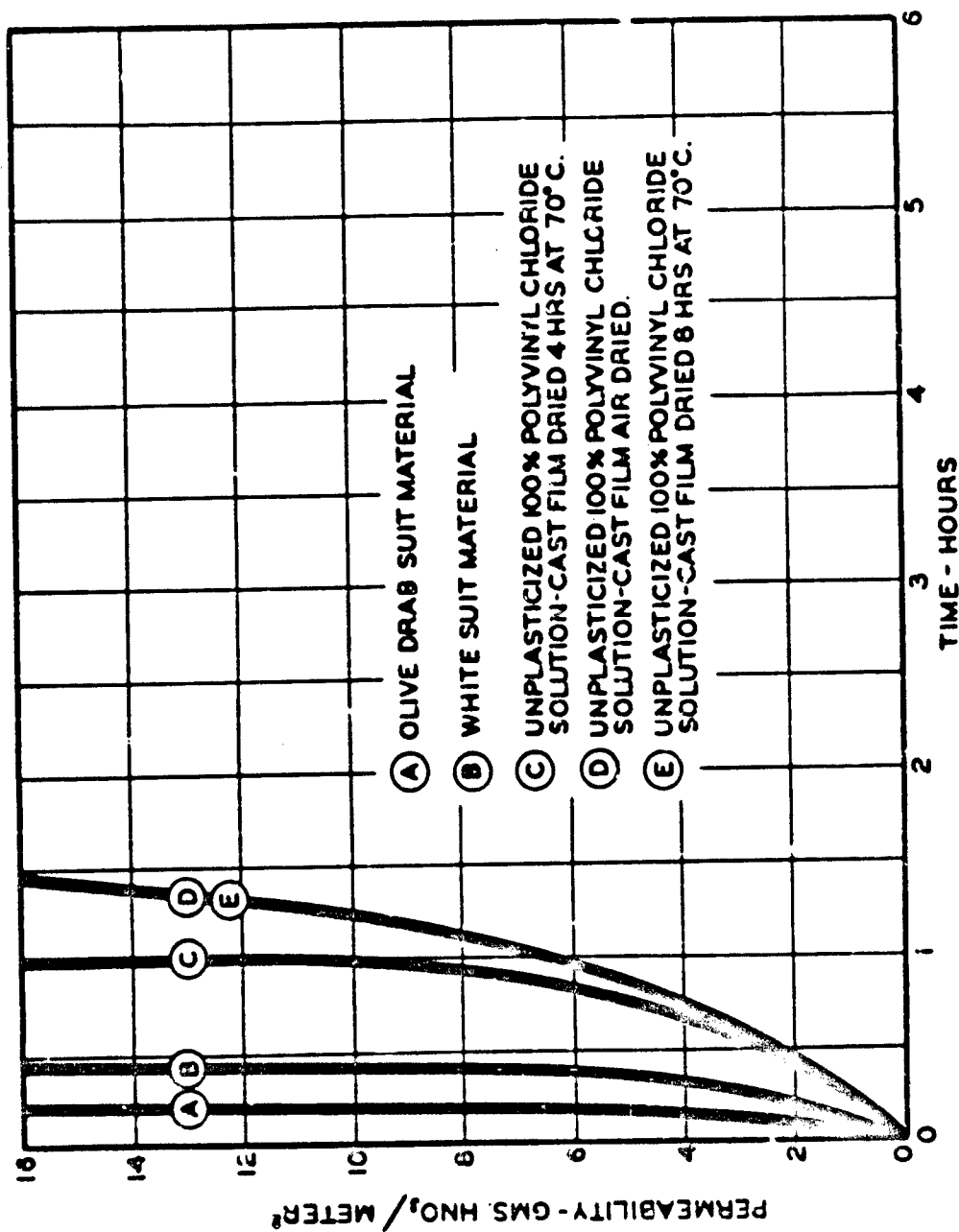
FIG.24 - NITRIC ACID PERMEABILITY OF VARIOUS POLYVINYL CHLORIDE MATERIALS.

(A) OLIVE DRAB SUIT MATERIAL

(B) WHITE SUIT MATERIAL

(C) UNPLASTICIZED 100% POLYVINYL CHLORIDE
SOLUTION-CAST FILM DRIED 4 HRS AT 70°C.

(D) UNPLASTICIZED 100% POLYVINYL CHLORIDE
SOLUTION-CAST FILM AIR DRIED.

(E) UNPLASTICIZED 100% POLYVINYL CHLORIDE
SOLUTION-CAST FILM DRIED 8 HRS AT 70°C.
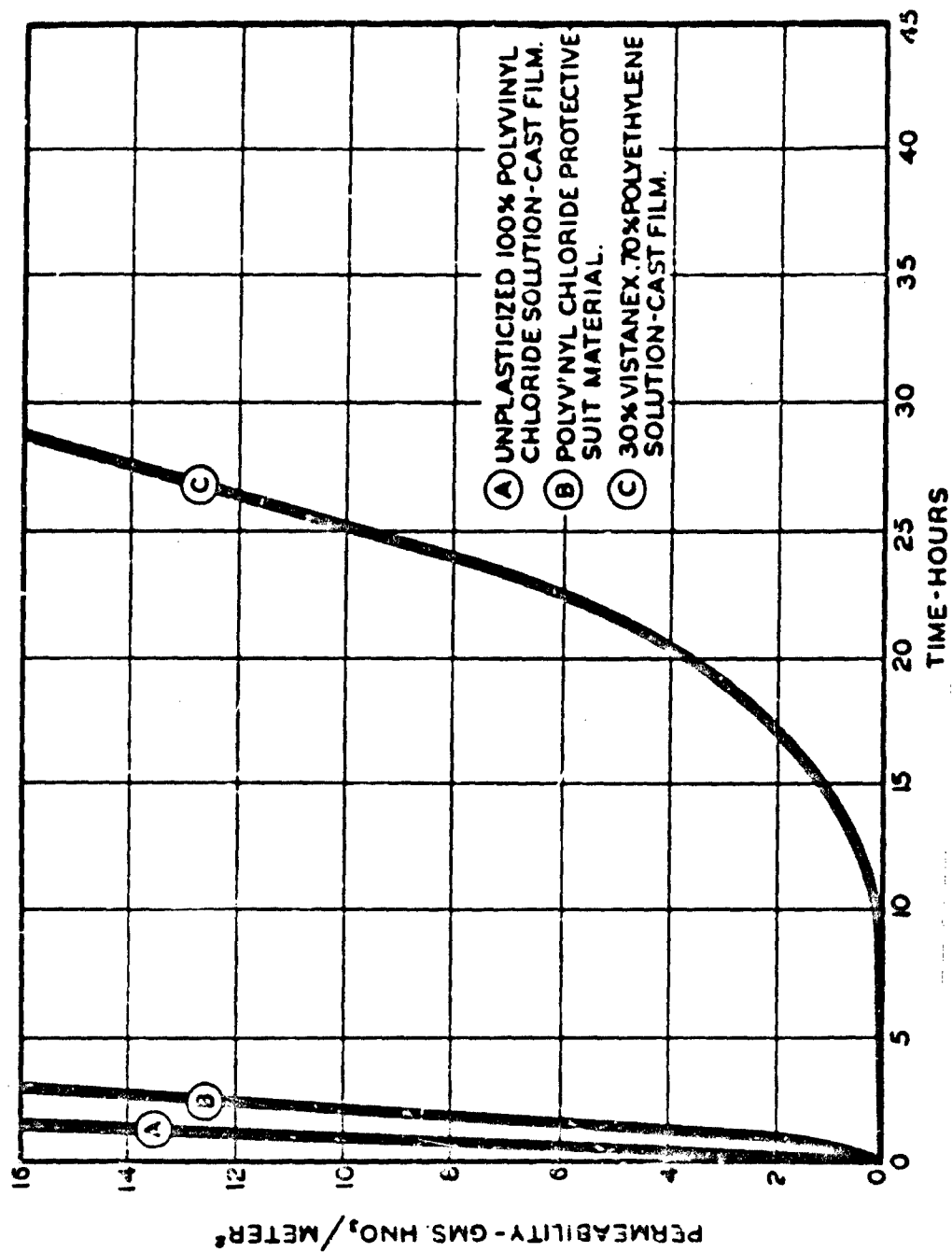
FIG. 25-NITRIC ACID PERMEABILITY OF POLYVINYL CHLORIDE MATERIALS
AS COMPARED WITH POLYETHYLENE-VISTANEX [70%-30%] SOLUTION-CAST FILM.

D. Glass Fabrics Coated With Kel-F

As was mentioned previously, Teflon and Kel-F possess excellent chemical resistance and reasonable flexibility, but they are lacking in physical strength, particularly tear-resistance. In order to improve the latter, a reinforcing fabric is necessary.

There are two methods in widespread use for the coating of fabrics with plastic coatings. The first, to convert the plastic to a liquid or semiliquid consistency and to spread it over the fabric and then cause it to resolidify, usually called coating. The other, to use a previously prepared film of the plastic and to adhere it to the fabric by means of a suitable adhesive, usually called laminating. The lamination of Teflon to glass fabrics is discussed in the Literature Survey, 3. Fluorocarbon Laminates.

In the case of Kel-F and Teflon, the chemical inertness and temperature-stability which are so advantageous from a use standpoint prove to be a definite handicap in processing. They do not soften at ordinary processing temperatures and therefore it is necessary to reach temperatures approaching their decomposition point before softening occurs. In the case of solvent spreading, no satisfactory solvents are available for these materials. Thus, the only satisfactory method of fluid coating is by means of dispersions of very small discrete solid particles in a suitable liquid.

The technique of using the dispersion is to spread a layer of the liquid over the surface to be coated and then allow the dispersion medium to evaporate, leaving a layer of particles held sufficiently strongly by attractive forces to keep them from falling off. In order to form a continuous film, the particles must be joined by fusing them. This imposes a limitation which has confined the experiments to glass cloth: namely, that the fusion conditions are far beyond the temperature at which fabrics made from organic materials decompose.

Initially, it appeared that a glass fabric could be coated with a layer of Teflon or Kel-F from a dispersion and the coating fused to make a continuous film. Fiberglas Cloth (108) was pretreated to remove the starch and binders, and four dip-coatings of 75 percent Kel-F dispersion (34% solids in xylol) and 25 percent silicone oil (9996-500) were applied. The cloth was passed through doctor blades after each coating, and fused at 510°F for 15 minutes. A final coating of plain Kel-F was then applied, and the whole was fused for 30 minutes at 510°F.

Addition of silicone oil did not enhance the flexibility.
Optimum results were obtained when each coating was fused
instead of semifused, as in the case of the Teflon dispersions.
Where oil was included in the coating compounds, the final
coating had to be plain Kel-F, or an extremely oily surface
resulted. The samples failed instantly when tested for nitric
acid resistance.

In an attempt to increase the resiliency, two samples were
made from a dispersion containing 20 percent silicone oil
and 80 percent Kel-F dispersion. The processing was similar
to the previous experiments, but only three coats were applied,
with a final coating of plain Kel-F. Final fusion was at
550°F for half an hour. This increased fusion temperature
gave a well-fused sample, but the resiliency was not improved.

The next experiment was to determine if the coating of one
side of the glass cloth would increase the nitric acid
resistance and flexibility. It was believed that by this
method there would be no possibility of entrapping air, which
results in porosity. The cloth was also lubricated before
coating to promote greater flexibility. Glass cloth (108)
was pretreated, then impregnated with DC35B (an aqueous
silicone oil dispersion), and semidried at 550°F for 30
minutes.

Four coatings (Kel-F dispersion, 90%, Silicone oil, 10%)
were applied to one side of the Fiberglas, each coating being
fused at 510°F for 15 minutes. Two final coats of plain
Kel-F were then added, and the sample was fused at 550°F for
30 minutes.

Lubricating of the fibers increased the flexibility, but
it was now definitely established that the addition of a
silicone oil to the coating dispersion was of no value in
this respect.

A leno-weave, marquisette-type fabric was then processed,
the silicone oil in the coating dispersion being replaced
by a Halocarbon wax (10-00). This fabric was dipped in the
mixture of Halocarbon wax and Kel-F dispersion, and the
excess coating was removed by doctor bars. When the sol-
vents had evaporated at room temperature, the coating
was fused at 480°F for 1 hour. The process was repeated
to obtain a continuous layer of Kel-F particles. The
fabric appeared to be well sintered and free of pin holes,
but was too stiff for clothing material, so acid-permeability
tests were not run.

In order to limit penetration of the dispersion into the fabric, and thus improve its flexibility, a Knowlton Table Coater was used to coat a number of different types of glass cloth on one side only. The glass fabric, as received, was tightly suspended across the coater. A mixture of one part Halocarbon wax (10-00) dissolved in toluene and two parts of Kel-F solids as a 32.7 percent dispersion in xylene, was poured on the upper side of the cloth. Excess coating was removed, and the thickness was regulated by drawing the scraper blade across the fabric. The solvents were allowed to evaporate at room temperature. The fabric was then suitably supported and placed in an oven at 480°F for one hour. Multiple coatings produced a film thickness of from .003 to .005 inch. The coatings were well adhered and continuous, but "papery" to the touch and unsatisfactory for wearing apparel. Nitric acid permeability tests were also unsatisfactory.

Of all the types of glass cloth investigated by this method, the greatest flexibility was obtained with a leno-weave, marquisette-type fabric.

As the fabrics prepared by the aforementioned methods possessed low resistance to nitric acid penetration, a technique was devised to cast a film on the fabric. A section of marquisette-type, glass fabric was placed on a glass plate, bordered with glass edging. Over this was poured a dilute mixture of Halocarbon wax Kel-F dispersion. Solvents were evaporated at room temperature, and fusion was accomplished at 480°F for two hours. Fabrics coated by this method were impregnated on only one side, and thus were quite flexible, but acid-permeability was unsatisfactory.

E. Glass Fabrics Coated with Teflon

Similar attempts were made to coat glass fabrics with Teflon. The coated fabric was made by thoroughly soaking a heat-treated glass cloth (Fiberglas 116) in an aqueous dispersion of Teflon (46% solids). The fabric was then manually drawn through scraper bars to remove the excess coating, and semifused at 610°F for 15 minutes. Six coats were applied in this manner, and the sample was finally completely fused at 720°F for 15 minutes.

The resulting fabric was stiff and boardy, and although the coating appeared to be continuous, subsequent tests showed poor acid-resistance, indicating microporosity. In an effort to improve the flexibility of the fabric, a silicone oil was added to the Teflon dispersion.

Experiments were conducted, using 50 and 20 percent silicone oil (9996-500) by volume with Teflon dispersions. Five coats were applied and semifused at 610°F. A sixth coating of plain Teflon dispersion was then added, and the whole was fused at 720°F for 15 minutes. The resulting fabrics were more flexible, but the surfaces were oily. Pinholes were visible in some cases where great amounts of oil had accumulated. Both fabrics failed to resist penetration of nitric acid.

It was thought that if a lighter-weight glass cloth were used, more resiliency would be imparted to the fabric. Fiberglas 112 as well as 116 were coated with Teflon dispersions containing 12 and 15 percent silicone oil. Three coats were first applied, as previously mentioned, with semifusing between coats, then the final three coats of plain Teflon dispersion were added in the same manner. The final fabric was fused at 720°F. Samples prepared with the lighter-weight cloths were more resilient, but still did not resist nitric acid.

Tests were then initiated, replacing the silicone oil with an aqueous dispersion of silicone oil. Fabrics were prepared, similarly to those mentioned above, but using 10, 12, 15, 20 and 25 percent of DC35B in place of the #9996-500. It was noted that oil globs were absent from the cloth because of compatibility with the Teflon dispersion, and the flexibility was improved. The number of coatings was reduced to four when it was noticed that an even lighter glass cloth (108) gave excellent "strike through" and a good continuous surface. The final fusion period was increased to 60 minutes, eliminating some of the pinholes and giving a

better fused sample. As a result of these various changes, the samples were capable of resisting fuming nitric acid for three hours.

In every case, the acid-resistance was not satisfactory, and it was concluded that unless new types of Teflon could be found, no further work would be done on this product.

F. Kel-F, Glass Fabric, Silicone Rubber Laminates

The previous section described dispersion methods for coating Fiberglas cloth with Teflon and Kel-F. Both dip-coating and skim-coating resulted in too great a penetration or even strike-through of the dispersions, resulting in boardy or inflexible fabrics.

In an attempt to keep the dispersions on the surface, glass fabrics were first primed with a silicone rubber, and then coated with Kel-F on a Knowlton Table Coater.

Cohrlastic, a product of The Connecticut Hard Rubber Company, is Fiberglas coated with silicone rubber. The Fiberglas side of this product was first cleaned with a rotating brush to remove any silicone which might have struck through, and was then placed on the coater with the Fiberglas side up. A modified Kel-F dispersion was poured on, and the fabric was coated. After drying, the fabric was fused for one hour at 480°F. Two samples were prepared in this way, one with four coats (Figure 26, Curve A) and one with five coats (Figure 26, Curve B). After the final fusion, the fabric was placed in an oven at 480°F for fifteen minutes. On removal, it was quenched in water at 20°-25°C to retain the flexibility of the Kel-F.

The use of a fabric, previously coated with silicone rubber, improved the flexibility, but the presence of a molecular film of silicone on the exposed side of the Fiberglas resulted in poor adhesion of the Kel-F to the fabric.

In an attempt to overcome this lack of adhesion, Dow Corning Silastic (C 125) silicone rubber, dissolved in toluene, was thinly applied to one surface of the fabric, and immediately inverted on the coater to prevent excessive strike-through. Curing of the fabric was done in the usual silicone cycle. The coated fabric was then coated on its glass surface with a plasticized Kel-F dispersion (one part Halocarbon wax 10-00: two parts Kel-F solids in xylene). The solvents were allowed to evaporate, and the fabric was fused at 480°F for one hour. Additional Kel-F coatings were applied in this manner. Various types of fabric, ranging from Grade #128 to #108 and leno weave were processed by this method. An improvement in flexibility was noted in all cases, but a decrease in adhesion of the Kel-F to the glass fabric resulted. No gain in nitric acid resistance was apparent, permeability values being of the same order as those determined for Kel-F coated fabrics without silicone rubber backing.
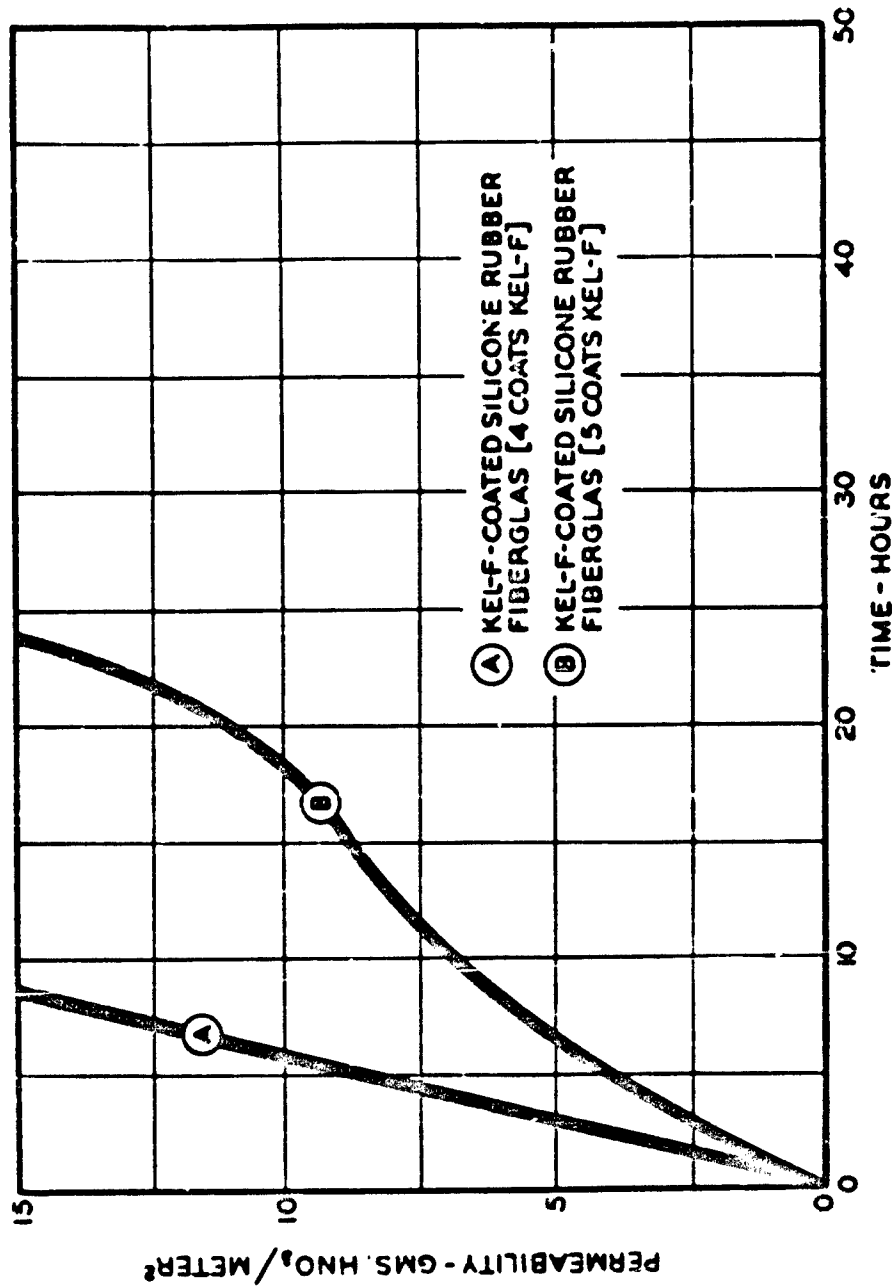
FIG. 26 - NITRIC ACID PERMEABILITY OF KEL-F-COATED
SILICONE RUBBER FIBERGLAS.

(A) KEL-F-COATED SILICONE RUBBER
FIBERGLAS [4 COATS KEL-F]

(B) KEL-F-COATED SILICONE RUBBER
FIBERGLAS [5 COATS KEL-F]

TIME - HOURS

PERMEABILITY - GMS. HNO_3/METER²

A number of similar experiments were then run in which
eight-mil films of plasticized Kel-F dispersion were cast
on the rubberized glass fabric. The Knowlton Coater was
used, but eight-mil shims were placed at the sides, the
knife being used to spread the films evenly. After solvent
evaporation, the fabric was fused at 480°F for one hour.

The films were well sintered and devoid of cracks, but no
improvement in flexibility over skim-coating was noted, and
nitric acid permeability was unsatisfactory.

At this point of the investigation, no satisfactory tech-
nique of coating from a dispersion had been developed.
Therefore an experiment was instituted to laminate plasti-
cized, extruded Kel-P films and Fiberglas.

G. **Lamination of Plasticized, Extruded Kel-F Film to Glass Fabrics**

A technique was developed by which an extruded, plasticized Kel-F film (Trithene) was laminated to a glass fabric. A satisfactory bond between the fabric and Kel-F film was obtained, and the acid-permeability of the fabric was comparable to that possessed by the unsupported film. Acid-permeability curves for two of these fabrics are presented in Figure 27.

The initial samples were obtained by laying an extruded Kel-F film over leno weave, glass fabric and heating the laminate in an hydraulic press at 350°F and 1500 psi for three minutes. Satisfactory material was also obtained by placing the Kel-F, glass fabric laminate between the rubber surfaces of two pieces of silicone rubber-coated glass cloth, applying a weight on the surface equivalent to one half pound per square inch, and heating to 480°F for three hours. A third method was to wrap a mandrel successively with a sheet of silicone rubber-coated glass cloth, a layer of Kel-F film, a layer of Fiberglas and a layer of silicone rubber cloth. The assembly was then wrapped with Fiberglas tape under slight tension and heated to 480°F for thirty minutes.

Fabrics produced by the above methods represent the minimum penetration of the coating material into the body of the fabric. Although these fabrics had the best flex characteristics of any Kel-F-coated glass fabrics which had been prepared, it was the opinion at Wright Field that they still lacked the flexibility and drape required for the fabrication of protective clothing.

At a conference with personnel of Wright Air Development Center on December 9, 1952, it was decided that in view of the relatively short exposure time anticipated in actual use, absolute acid-resistance should be compromised for greater flexibility. As a consequence, all efforts were concentrated on developing fabrics coated with polyethylene-polyisobutylene blends.
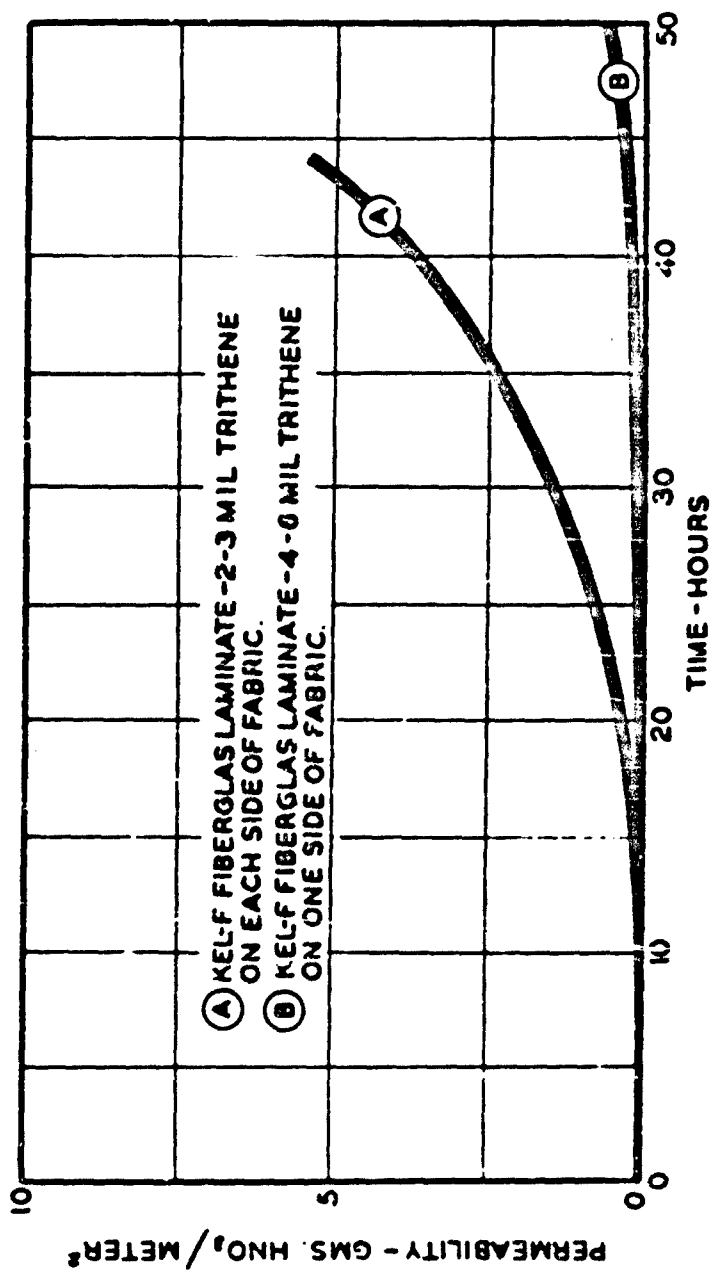
FIG.27-NITRIC ACID PERMEABILITY OF KEL-F-FIBERGLAS PRESS-LAMINATED FABRICS.

LITERATURE AND PATENT SURVEY

A. Literature Survey

1. Permeability

Simril and Hershberger (11) have written a very fine report on their permeability studies of sixteen polymeric films to organic vapors, together with a clear summary from previous literature of the mechanism of and factors affecting permeation. Their data record permeability constants as measured in Thwing-Albert vapometer cups and are defined as moles of vapor passing through one square centimeter of film having a thickness of one centimeter per second per centimeter (Hg) vapor pressure difference across the film. Although the permeability of vapors is of some interest, a major concern is the permeability of films to liquids, particularly to fuming nitric acid. Their testing methods and specific results need not be discussed further.

The authors summarize the theory of the mechanism of the diffusion of small molecules through membranes as involving three processes: passage of small molecules through preformed holes or capillaries; diffusion of small molecules through temporary holes formed as a result of thermal motion in the polymer chains; and diffusion resulting from the interaction of diffusing molecules with active spots in the film. In the last of the three, a diffusing molecule attaches itself to an active spot where it vibrates until it acquires sufficient energy to break loose and traverse farther to another active spot or on through the film. The authors conclude that the first method is of little importance in well-formed films. They state that hole formation and therefore diffusion is increased in compounds containing bulky and nonpolar side groups. Permeation can be expected to be greater where the film and the diffusing molecules have similar structure, particularly regarding polarity, because they dissolve each other more readily. The presence of polar groups reduces the solubility of a nonpolar gas in an organic liquid, and, conversely, polar gas molecules dissolve more readily in a liquid with polar molecules than without polar molecules (3). Simril and Hershberger also found some correlation between permeability and dipole moment.

Polymers having strong interchain bonding forces (such as nylon) exhibit low permeability, as one would expect because there are fewer holes. Increases in temperature, of course,

increase thermal motion of the polymer chains, and therefore increase the rate of diffusion.

The effect of the addition of a plasticizer to the film compound may either increase or decrease the permeability. An increase in permeability may be due to increased ease of hole formation or to an increase in the solubility of the diffusing molecule in the film. A decrease in the permeability can be brought about by a lessening either in hole formation or solubility. If the plasticizer is similar in molecular structure to the diffusing material, the latter will probably be soluble in the film and diffusion will thus be greater.

Myers and Phillips (6) state that solvents which do not attack or dissolve a plastic may still migrate through it at an appreciable rate. This rate is dependent on the properties of the solvent and the membrane. Myers and Phillips conducted a study of the transmission rates of many organic liquids through polyethylene film, neoprene, polyisobutylene and several other materials. Polyethylene was found to be superior in general, as regards impermeability. The transmission rates of polar and nonpolar compounds were found to be inversely proportional to film thickness, and directly dependent on time and an exponential function of temperature. The transmission of the organic vapors was considered to be an activated diffusion process, and conformed to the fundamental diffusion laws for fixed gases through organic high-polymer films.

Peirls (9) points out that polyvinyl alcohol plastics are entirely unaffected by gasoline and oils, but are not resistant to acids or alkalies. Houwink (4) states that the permeability in high polymers of gases or liquids depends on the product of the solubility and the coefficient of diffusion. Stout, Geisman and Mosley (12) state that two factors affect the permeability of elastomers: solubility of the gas in the polymer, and the diffusivity within the polymer.

2. Properties of the Fluorocarbon Polymers

The class of fluorocarbon polymers exhibits a unique combination of properties: high heat-resistance, great stability and chemical inertness, excellent electrical insulating

characteristics, noninflammability, no water absorption, high humidity-resistance, and "fungi inertness," i.e., natural resistance to fungus growth, states Javits (5). Though the materials are expensive on the basis of price per pound, they are more economical in many applications than previously used materials because they have such long life and because they often allow the over-all size of equipment to be reduced.

The two important fluorocarbons are: polytetrafluoro-ethylene and polymonochlorotrifluoroethylene. The former has been developed by duPont under the trade name of Teflon, and the latter is known commercially as Kel-F (M.W.Kellogg Co.) and Fluorothene (Carbide and Carbon Chemicals Corp.).

A cautious comparison of the two would reveal that Teflon has somewhat superior electrical properties and higher heat-resistance, whereas Kel-F has somewhat superior physical properties. Schildknecht (18) discusses the fluoro-vinyl polymers.

Teflon Physical Properties

According to Javits (5), Teflon's thermal stability can be considered as 250°C for most uses. At this continuous temperature, it loses only about one percent of its tensile strength per month. DuPont chemists consider that it can serve in special applications at temperatures up to 300°C, though in tests it loses 10 to 20 percent tensile strength per month at this temperature. It does, however, exhibit undesirable changes under temperature extremes, such as relatively high thermal expansion and undesirable cold flow.

Teflon Chemical Properties

There is no known solvent for Teflon over the temperature range from minus 195°C to above 327°C, its sintering temperature. It is attacked only by molten alkali metals and by fluorine and chlorine trifluoride at high temperatures. It is chemically resistant to all concentrated acids including fuming nitric acid. There are no detectable changes after continued weathering for four years (Fla.), and the water absorption is 0.0 when tested according to the A.S.T.M. method.

Teflon Mechanical Properties

The tensile strength of Teflon is not particularly high
(1500 to 2500 psi), though in oriented film it has been
recorded as high as 15,000 psi. It undergoes instantaneous
deformation under compression, and has excellent elastic
memory if reheated to its transition temperature.

Its solid-phase transition point is sharply defined at
327°C, at which temperature it becomes an amorphous gel.
At 400°C, it begins decomposing to the gaseous monomer.
When Teflon decomposes, gaseous fragments break off at the
ends of the polymer chain. This is in contrast to what
happens to Kel-F, in which case the chain breaks in or
near the middle.

Minnesota Mining and Manufacturing Company (10) of St.Paul,
Minnesota, report of their "PTF" film, made of duPont
Teflon, that its physical properties are stable from -100°F
to 500°F, and that it has excellent resistance to cold
flow under pressure, low shrinkage, and good elastic memory.

The numerous duPont Technical Bulletins about Teflon, put
out by the Polychemicals Department, report these same
properties.

Kel-F Physical Properties

This polymer has four-fifths of its weight in the two
halogens, fluorine and chlorine. Kel-F has thermal stability
to a continuous temperature of 175° to 200°C. It exhibits
less cold flow under compression than does Teflon and has
very good recovery without reheating. Its thermal expansion
is less than that of Teflon, but at 200°C it has no flexural
strength (5).

Kel-F Mechanical Properties

The tensile strength of unoriented Kel-F is 5,700 psi, and
in oriented film it reaches as high as 30,000 psi. Oriented
film is a film that has been stretched to a fine thin strip.
This renders the long-chain molecules closely aligned
parallel to one another, whereas in the original unoriented
film they are in random arrangement. The hardness of Kel-F
can be varied considerably from soft and resiliant to tough
and rigid without loss of stability, merely by varying the
heat treatment. Quenching, rapid cooling from 425° to
300°F, increases flexibility and transparency (7). The

degree of opaqueness also varies with the heat treatment.
Kel-F shows some crazing at low temperatures (5).

It has superior molding characteristics, being easily
molded by compression, transfer, injection, or extrusion.
The molding temperature must be carefully controlled,
however, since at 315°C it starts to degrade (5). Dimensional
stability is assured by annealing for 24 hours at 255°F (7).

B.H.Maddock (15) of Union Carbide and Carbon Corporation
has discussed the extrusion of Fluorothene film in some
detail. The properties of the film are surveyed, and it
is shown that straight die extrusion and very rapid
quenching of flat film produce improvements in clarity,
flexibility, and low-temperature brittleness. The film
is more satisfactory than that obtained by air-cooled
tubular extrusion which cools the film rather slowly. The
improvement can be directly attributed to reduced
crystallinity.

F. Dexter (16) has outlined several methods of resin class-
ification by plasticity tests. A brief outline of the
theory of flow of molten polymers is given, along with a
general discussion of the evaluation of such plasticity
data. A survey of the parallel plate melt viscosity and
No Strength Temperature (NST) is included, and another
test similar to the Melt Index Test used with polyethylene
is described. (The M.W.Kellogg Company has recently announced
a superior method of testing Kel-F, which is called the ZST
Test).

W.J.Merck (17) has outlined the design and test procedures
used in making nitric acid expellant bags and the elimina-
tion of folds and wrinkles which eventually cause leaks.
This was accomplished by proper design of the bladder.
Several photographs and diagrams are included which clarify
the design problems.

Kel-F Chemical Properties

Kel-F is chemically inert, for all practical purposes. It
is unaffected by organic solvents and has good weathering
resistance (5). It is resistant to concentrated acids,
including fuming nitric acid (6). It is slightly swelled
and plasticized by highly halogenated materials and some
aromatics (6).

3. Fluorocarbon Laminates

Javits (5) reports that successful laminates to glass fabrics have been made which incorporate all the desirable properties of the polymer. The impregnated fabrics have been produced in continuous rolls. Laminates can be compounded into heavier structures. Javits also states that some work was being done at the time of writing (1950) with development of Kel-F laminates.

The Polychemicals Department of duPont (13) reported early in 1952 that many porous structures have been impregnated with Teflon dispersions. They state that, basically, lamination merely consists of casting a film on a discontinuous surface. They have made baked coatings on woven glass or asbestos fiber cloth. In order to build heavy homogeneous coatings, it is necessary to make multiple dippings, with baking between. Soluble electrolytes should be washed out of the fabric before coating with Teflon, because their presence might coagulate the Teflon. Strong laminates can be made by stacking the impregnated fabrics and then baking under pressure at 675° to 700°F. Less heat-resistant fabrics can also be laminated by successive dipping and drying operations without sintering. Application of pressure before or after each drying improves these laminates.

Visking Corporation (14) reports successful lamination of Trithene (Visking's film of monochlorotrifluoroethylene polymer) to glass fabric, cloth and canvas batting, stainless steel, aluminum, and metal screen cloth.

4. Chemically Resistant Protective Clothing

Visking Corporation (14) suggests that Trithene be used to fabricate chemically resistant safety clothing.

Allison (1) has reported experiments to find a high saturation elastomer for use in protective clothing for chemical exposure. He concludes that of the materials tested, butyl rubber and butyl-Vistanex blends show the highest chemical resistance. Three types of resistance tests to fuming-type acids were used: (1) total immersion as a screening test, (2) static penetration, and (3) dynamic penetration. In the latter two, an indicator on the other side of the film was used to show the presence of acid vapors. Test results were given as the time in minutes until sufficient vapors

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penetrated the film to affect the indicator. In the total
immersion test, butyl rubber was found to be superior to
Kel-F and polyethylene plastics. The Kel-F tested was
unsupported film, and the Teflon was gasket material and
laminated Fiberglas cloth. In the static penetration test,
it was found that failure time varied linearly with
increasing number of layers thickness of the specimen.
Schildknecht (18) discusses extensively the chemical and
physical properties of both polyethylene and Vistanex.

B. Patent Survey

The following United States patents deal with the manu-
facture and compounding of chlorotrifluoroethylene polymer.

U.S. Patent 2,531,134 (18) Dimethyl Phthalate Solution of
Acetyl Peroxide as Catalyst for Trifluorochloroethylene
Polymerization (11-21-50).

E. L. Kropa and J. J. Padbury of American Cyanamid Company
have developed methods of making halogen-substituted
ethylenes, particularly trifluorochloroethylene, and polymer-
izing them to readily molded and shaped polymers. Processes
for obtaining high yields of the high-molecular-weight
polymers were developed.

U.S. Patent 2,600,802 (19) obtained by the M.W.Kellogg
Company, deals with plasticized trifluorochloroethylene
polymer

U.S. Patent 2,600,804 (20) Production of Chlorotrifluoro-
ethylene Polymer-In-Monomer Slurry (6-17-52).

J.S.Rearick of the M.W.Kellogg Company has developed a
"continuous process for the polymerization of polyfluoro-
olefins to produce normally solid polymers." He has
developed an improved manufacturing process and apparatus
that will control more closely the reaction temperature
of the polymerization and improve the "quantity and
reproducibility" and increase the yield of normally solid
polymers of trifluorochloroethylene.

The monomer for polymerization, a perfluorochloro-olefin,
is obtained by dechlorinating a saturated perfluorochloro-
carbon in the presence of a metal halide. Substantially

pure liquid monomer, recovered from a fractional distilla-
tion system, is polymerized with a suitable catalyst, under
agitation. A slurry of the solid polymer and liquid
monomer results. A portion of the slurry is continuously
being removed and filtered to recover the solid polymer
in powder or granular form. The entire process is a con-
tinuous one in which unused portions of the various agents
and reactants are continually recovered and returned to the
system. (This method is presumably being used in Kellogg's
new plant.)

U.S. Patent 2,600,82. (21) Process for Polymerizing
Trifluorochloroethylene (6-17-52).

J.M.Wrightson of the M.W.Kellogg Company has developed a
method to remove the heat produced by polymerization of
trifluorochloroethylene during the reaction, controlling
the reaction temperature adequately, and improving the
quality of the solid polymers produced. According to this
method, liquid diluent present during the polymerization
of trifluorochloroethylene is evaporated during the reaction,
and the heat of polymerization is thus removed as latent
heat of vaporization.

U.S. Patent 2,600,202 (22) Method for Polymerizing
Chlorotrifluoroethylene (6-10-52).

D.W.Caird of the General Electric Company has developed a
process for making a substantially heat-stable, high-
molecular-weight chlorotrifluoroethylene polymer by
agitating an aqueous suspension of a mixture at below pH-5
in the presence of ultraviolet light. The aqueous mixture
contains chlorotrifluoroethylene and a water-soluble,
inorganic peroxide polymerization catalyst for it, boric
acid, a water-soluble iron salt, and a reducing agent
readily oxidized in the presence of the polymerization
catalyst and the iron salt.

U.S. Patent 2,599,640 (23) Copolymers of Chlorotrifluoro-
ethylene, an Olefinic Hydrocarbon and a Vinyl Carboxylate
(6-10-52).

R.M.Joyce, Jr., of the duPont Company has accomplished the
preparation of new high-molecular-weight polymers and of
compositions containing them, by polymerizing a mixture of
chlorotrifluoroethylene and a vinyl ester of an organic acid
such as vinyl acetate in the presence of a peroxy catalyst such
as benzoyl peroxide.

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23. Caird, David W. Method for Polymerizing Chlorotrifluoroethylene. Application date 28 June 1950. U.S. Patent 2,600,202.

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A P P E N D I X

TABLE 1

NITRIC ACID PENETRATION OF VARIOUS SAMPLES (gm/ft²)

SAMPLE (NOTE)	1 A	11 A	111 C	1V A	V D	V1 D	V11 A
PU.VISTANEX B-80	20	-	-	20	-	-	50
PU.POLYTHENE LE13	20	100	100	20	-	-	50
Time – Hours							
0.5	.005	.005	.019	.005			.013
1	.005		.030	.017			.013
2				.25	.1		
3					.3	.016	
4		4.5	.061		.6	.27	
5					1.2	.70	
5.5					1.9	1.4	
6					2.5	2.0	
7.5					3.9		
10					10.0		
12	12.0		6.8	130.0		6.7	1.4
14			8.2			16.0	5.3
18	30.0	390	20.0				8.0
20		850	44.0				
25		Note B	109.0				
30							
45							
55							

Notes:
A – Solution – Cast Film
B – Greater than 1000 gm/ft² HNO₃
C – Pressure-Molded Film
D – Sample of Suit Material produced by the U. S. Rubber Company

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TABLE 2

NITRIC ACID PERMEABILITY OF SOLUTION-CAST POLYURETHANE-POLYETHER
B-40 FILMS OF .006 - .007 INCHES THICKNESS (gms/ft²)

SAMPLE NO.	1	11	111	1V	V	V1	V11	V111	1X	X	X1	X11
PER.THICKNESS x10⁻³	90	80	70	70	50	60	60	60	70	70	80	90
PER.PERMEABLES	11	90	80	60	50	60	60	70	90	80	90	

Time - Hours												
0.5	.014		.049	.022	.019		.047		.025	.047	.017	.035
1	.035	.049			.022	.035		.035	.017		.12	1.20
2	.035	.039	1.7		.035	.035	.05	.075	.075	1.0	7.0
3	.20				.04			4.4			
4	.28	3.70	10.6	4.4	.089	2.2	2.0	10.0	10.0	100.0
5	.43	14.0	118.0	230.0	.089	3.1	3.1	85.6	86.0	130.0
6	1.20			504.0	.72	5.5	5.6	52.0	118.0
7.5	5.60				1.80	85.0	8.4
20	22.0				3.6	10.0	30.0
21						10.0	34.0
25	40.0				7.0	66.0	40.0
29	66.0				16.0		60.0
52							100.0
72	126.0		

TABLE XI

NITRIC ACID PERMEABILITY OF PRE-SIZED POLYETHYLENE BOTTLES
(W/E.J.) OF THE PICKLE

SAMPLE NO.	113	132	111	114	110	111	117	128	127	116	124	119
PSI. VISTANEX D-50 100	-	90	80	70	80	90	90	60	70	80	90	100
MIS. POLYETHYLENE	100	10	80	80	70	80	90	80	80	80	10	100

Time-Hours												
0.5	.030	.04	.04	.016	.025	.04	.030	.04	.035	.035	.035	.019
1	.035						.035		.035	.035	.035	.030
1.5	.035	.04		.04	.090	.022		.04				
2				.04		.030			.04	.047	.047	.04
4	1.4	.080	.04		.04	.04	.04	.04	.47			
5				.022	.047	.047		.27	.70			
6		.105	.047		.055	.074				1.2	2.5	6.00
22	5.3	.30	.022	.075	.055	.12	.04	.54	1.4	3.0		
24	8.2				.090						5.6	8.20
25	40.0	.17	.075	.105	.12	.27	1.0	1.2	5.6	11.2		20.0
26			.105		.23	.27	2.0	1.7	5.6	11.2	34.0	
30	66.0	.84	.20	.20	.27	.68	3.0					66.0
45		2.0	.28	.28	1.2	1.7		6.9	20.0	68.0		
48			.70	.70	1.7	2.0	13.6					109.0
50		.124	1.4	1.4	2.0	2.0					116.0	
55			5.6	5.6	3.1	3.1						
48					5.6	5.6						

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TABLE 4

NITRIC ACID PERMEABILITY OF PRESS-BOUND POLYETHYLENE-VISTANEX

mg NO₂ DIFFUSED PER HR. OF SAMPLE THICKNESS (mg/hr)

Time-Hours	1 207	11 205	111 205	V 211	V 207	VI 211	VI 151	VII 207	IX 208
PTS.VISTANEX B-100	70	80	80	40	80	60	80	80	70
PTS.POLYETHYLENE	20	20	80	60	20	20	50	20	30
PTS.VISTANEX B-120									
.5	.030	.035	.030	.025	.030	.040	.040	.040	.80
2	.035	.030	.080	.030	.085	.040	.040	.020	.20
4	.055	.064	.090	.090	.105	.105		.020	
5.5	.11	.12	.20	.12	.56	.17		.11	.23
22.5	.36	.27	.28	.13	.56	.17		.23	.10
28	.44	.33	.35	.15	2.0	.20	.48	.68	.68
30			.54	1.0	2.0	.20		.20	2.5
48				2.0			.56		2.5
54	1.4	.56					.45		
96		.70	2.0	10.0	8.4	.70	6.4	7.0	12.0
100	1.4	1.2	3.0	7.0		.80	8.4	6.4	20.0
117	2.0	2.0	5.6	13.0	8.4	2.0	16.0	10.0	25.0
119	3.5		10.0	13.0	16.0	5.6	16.0	16.0	
121	3.5		34.0			5.6		25.0	
113									
168							85.0		32.0
192									
214									
272									

TABLE 5

NITRIC ACID PERMEABILITY OF PRESS-MOLDED FILMS (.005 in.) USING HYFLON B-2 (mg/M^2)

TABLE 6

NITRIC ACID PERMEABILITY OF VARIOUS POLYVINYL CHLORIDE MATERIALS (gms/M²)

SAMPLE (Note):	I (A)	II (B)	III (C)	IV (D)	V (E)	VI (F)
Time-Hours						
0.125	4.0	1.5	-	1.0	1.0	-
0.25	>100	3.6	1.0	-	-	-
0.375	-	7.0	-	2.5	2.5	-
0.5	-	>100	2.5	4.5	4.5	-
0.75	-	-	5.2	7.2	7.2	2.0
1.0	-	-	11.5	11.0	11.0	-
1.25	-	-	-	17.0	17.0	-
1.5	-	-	-	-	-	-
2	-	-	-	-	-	9.0
3	-	-	-	-	-	15.5

Note:

A - Sample of Olive-Drab Suit Material.

B - White Suit Material.

C - Solution - Cast Film of Unplasticized Polyvinyl Chloride, dried 4 hrs. @ 70°C.

D - Solution - Cast Film of Unplasticized Polyvinyl Chloride, air dried.

E - Solution - Cast Film of Unplasticized Polyvinyl Chloride, dried 8 hrs. @ 70°C.

F - Sample of Polyvinyl Chloride Suit Material.

TABLE 7

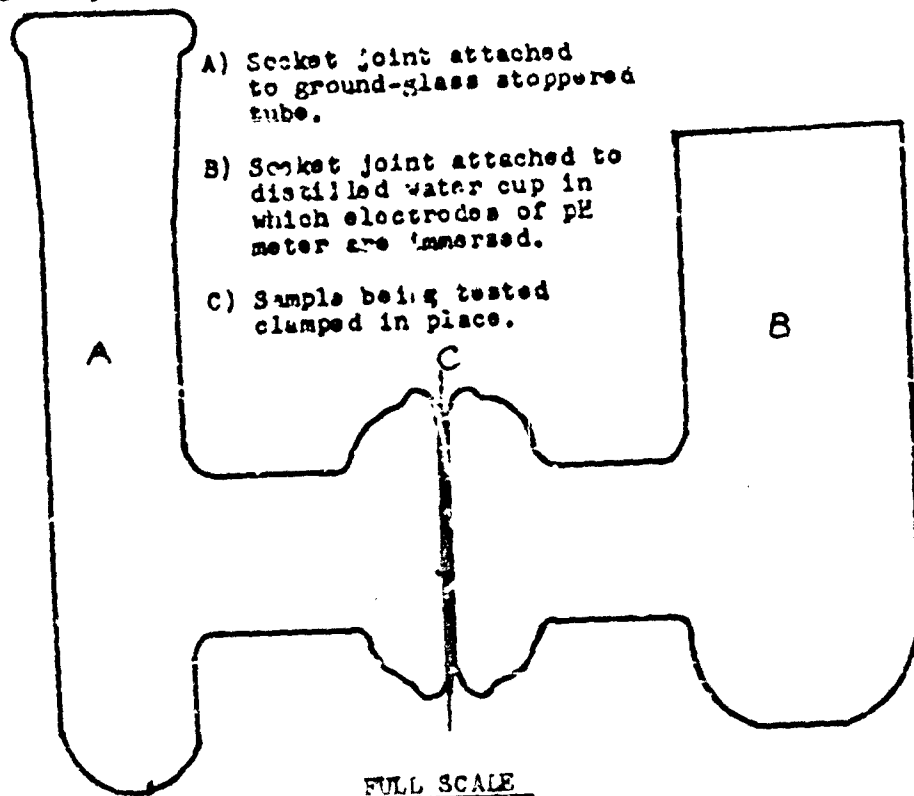### EFFECT OF FLAME-RETARDANTS ON FLAME-RESISTANCE OF POLYETHYLENE-VISTANEX BLENDS

Retardant	Parts	Total Pts. Retardant	Base Blend	Result
ZnO Bi$_2$O$_3$	10 10	20	80 pts. Vistanex 20 pts. Polyethylene	Burns Completely
ZnO Bi$_2$O$_3$	20 20	40	80 pts. Vistanex 20 pts. Polyethylene	Burns Completely
P-33	70	70	30 pts. Vistanex 70 pts. Polyethylene	Burns Completely
Kel-F Wax #150	5	5	80 pts. Vistanex 20 pts. Polyethylene	Burns Completely
Kel-F Wax #150	10	10	80 pts. Vistanex 20 pts. Polyethylene	Burns Completely
TiO$_2$	40	40	30 pts. Vistanex 70 pts. Polyethylene	Burns Completely
TiO$_2$	70	70	30 pts. Vistanex 70 pts. Polyethylene	Burns Completely
Sb$_2$O$_3$	70	70	80 pts. Vistanex 20 pts. Polyethylene	Burns Completely
Sb$_2$O$_3$ NH$_4$Cl ZnBO$_3$	25 25 25	75	80 pts. Vistanex 20 pts. Polyethylene	Burns Completely
			80 pts. Vistanex 20 pts. Polyethylene	Burns Completely
			30 pts. Vistanex 70 pts. Polyethylene	Burns Completely
			80 pts. Vistanex 20 pts. Polyethylene, calender-coated onto Dynel Fabric	Burns in contact with flame. Not self-extinguishing
			80 pts. Vistanex 20 pts. Polyethylene, calender-coated onto Dynel Fabric	Burns in contact with flame. Not self-extinguishing
TiO$_2$	40	40	80 pts. Vistanex 20 pts. Polyethylene, press molded onto Dynel Fabric	Does not burn when removed from flame
TiO$_2$	40	40	80 pts. Vistanex 20 pts. Polyethylene, press molded onto Vinyon Fabric	Intermediate between 13 and 14. Has slight tendency to be self-extinguishing

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<u>PROCEDURES</u>

Procedure A: Method for Determining Permeability to Fuming
            Nitric Acid

I. Description of Apparatus (H-Cell)

A) Socket joint attached
   to ground-glass stoppered
   tube.

B) Socket joint attached to
   distilled water cup in
   which electrodes of pH
   meter are immersed.

C) Sample being tested
   clamped in place.

<u>FULL SCALE</u>

II. Procedure

The sample to be tested is clamped between the two cells with
a ball-and-socket clamp, employing a butyl rubber gasket. One
hundred cc. of distilled water are pipetted into the distil-
led water cup, and an initial pH reading is taken by dipping
the electrodes of the Beckman pH meter into the distilled
water cup. Fuming nitric acid is poured into the ground-glass
stoppered tube, and pH readings are taken until the meter
registers pH 2.0 (arbitrary stopping point). A calibration
curve previously prepared, Figure 1, is used to find the acid
permeation rate in grams per square meter equivalent to the
pH readings.

Procedure 3: Preparation of Films from Various Blends of Polyisobutylene and Polyethylene by the Solution-Casting Method

A thirteen percent solution (by weight) of polyisobutylene (Vistanex B-80) in toluol was prepared by adding pieces of milled polymer to warm solvent with continuous stirring. Portions of this solution were weighed into containers where calculated amounts of polyethylene (Alathon A) were added to give the following blends:

A. 70 parts Vistanex B-80, 30 parts Alathon A
B. 50 parts Vistanex B-80, 50 parts Alathon A
C. 30 parts Vistanex B-80, 70 parts Alathon A

A homogeneous blend of the two polymers was obtained by warming the mixtures at temperatures of 100-120°C, with stirring. Solutions were maintained at this temperature for casting use.

Casting of films was done on glass plates which had been pre-heated to prevent precipitation of polyethylene during the operation. Solvent evaporation was carried out at 100°C for the same reason. The glass plates were edged with strips of glass which prevent flowing and distortion during film formation.

A portion of the thirteen percent Vistanex solution was used to prepare a film of pure Vistanex which was cast on a glass plate and allowed to air-dry overnight.

Procedure C: Preparation of Polyethylene Films by the Solution-Casting Method

Fifteen grams of polyethylene (Alatnon A) were placed in a flask containing 250 cc. of toluene. The flask was warmed on a steam bath, and the contents were agitated to bring about solution. The films were cast by pouring the warm solution onto warmed glass plates, and the plates were placed in an oven at 110°C. It was necessary to keep the temperature of the solution above 80°C at all times to prevent precipitation of the thermoplastic. Such precipitation increases the tendency of the film to crack when the solvent is evaporated. The films were allowed to remain in the oven for two hours to insure complete solvent evaporation and to allow each film to flow together to form a continuous sheet.

Procedure D: Preparation of a Polyethylene Film by
the Calendering Method

The rolls of the laboratory mill were heated by allowing a
batch of natural rubber to mix for 20 to 30 minutes, with
the cooling coils shut off. A portion of polyethylene
(Alathon A) was placed on the rolls and allowed to mix
for 15 to 20 minutes until it had banded and become soft.
The batch was sheeted off the rolls and allowed to cool.

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Procedure E: Preparation of Films from Various Blends
               of Polyisobutylene and Polyethylene by
               the Solution-Casting Method, Followed by
               Extended Drying

It is necessary to maintain the solutions at 150°-212°F and to
cast films on preheated glass plates. A complete series of
polyethylene-polyisobutylene (Vistanex) films was cast from
toluene solution. Calculated amounts of polyethylene and
Vistanex solution (previously made up to 11% in toluene)
were placed in Erlenmeyer flasks which were heated in boiling
water. Additional toluene was added, as required, to give
homogeneous solutions of a viscosity approximately equal
to that of SAE No. 10 oil.

A small portion of hot solution was poured on a glass plate,
preheated to 150°F. The hot solution was spread to a thick-
ness of .003 inch with a Bird applicator, and the plate
was placed in an oven at 150°F for 30 minutes. The plate
was then removed from the oven, and additional coats were
applied and dried, as before, until the films were .006
to .007 inch thick. After application of the final coat,
the films were held 5 to 6 hours at 150°F to remove as
much residual solvent as possible.

Procedure F: Preparation of Films from Various Blends
of Polyisobutylene and Polyethylene by
the Press-Molding Method

A complete series of polyethylene-Vistanex B-80 blends
was mixed on a hot mill (160°F) to a homogeneous state.
After milling, the batches were sheeted from the mill
and prepared for press-molding. A sample of the sheeted
film, about 3 in. by 3 in., was cut from the batch and
placed between two Teflon-covered (.002 in. shaved Teflon
film) aluminum plates (6 in. by 6 in. by 0.25 in.). (The
Teflon acts as a mold-release agent, simplifying the removal
of films after pressing.) The "mold" was placed in a press
at 280°F and was allowed to remain there for 15 minutes under
zero pressure. The preheating effectively softens the
blend to an easily molded plastic mass. After 15 minutes,
65 psi was applied to the plates for 5 minutes. Immediate
cooling under pressure was necessary to reduce bubbling and
to decrease the tackiness of the films before handling.
The standard thickness of .008 in. was obtained by the use
of metal shims of this thickness, which separated the plates.

<u>Procedure G</u>: <u>Determination of Flame-Resistance</u>
(List of Flame-Retardants on Page 26)

<u>Method A</u>. Flame-retardants were added to previously milled
blends of Vistanex and polyethylene, on a laboratory mill
heated to a temperature of 170°F. After complete dispersion
of ingredients, compounds were sheeted off the mill and sliced
into small rectangular sections. Each section was brought
into direct contact with a flame (approximate temperature,
180°F) and the amount of flaming was noted.

<u>Method B</u>. A blend consisting of 80 parts Vistanex and 20 parts
polyethylene, with an additional 40 parts titanium dioxide,
was prepared on the mill. After being sheeted off the mill,
sections were placed over Vinyon and Lynel fabrics. The
components were placed between Teflon-covered (.002 in.
shaved Teflon film) aluminum plates(6 in, by 6 in. by 0.25
in.) and then put in a hydraulic press which had been pre-
heated for 5 minutes at 280°F. They were pressed for 15
minutes at 65 psi. After being cooled under pressure, the
resultant coated fabrics were brought into contact with a
flame (approximate temperature 100°F) and their degree of
flammability was noted.

<u>Method C</u>. Previously milled, unfilled blends of polyethylene
and Vistanex were calendered on Dynel fabric. The flame-resis-
tance of the coated fabric was noted by placing a specimen
in direct contact with a flame (approximate temperature,160°F).

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Procedure H: Determination of the Degree of Blocking
of Coated Fabric Specimens

Test Samples: The following 1 in. by 1 in. specimens, processed to an over-all thickness of .015 in., were used for testing.

1. Vinyon Fabric (#501), calender-coated with a blend of 50 parts Vistanex B-80 and 50 parts Alathon A.

2. Vinyon Fabric (#501), calender-coated with a blend of 60 parts Vistanex B-80 and 40 parts Alathon A.

3. Vinyon Fabric (#501), calender-coated with a blend of 70 parts Vistanex B-80 and 30 parts Alathon A.

4. Dynel fabric, calender-coated with a blend of 80 parts Vistanex B-80 and 20 parts Alathon A.

Method: Four specimens of each type of coated fabric were superimposed to obtain three possible surface combinations (coating to coating, coating to backing, and backing to backing). Each composite was placed between two Teflon-covered (.002 in. shaved Teflon film) aluminum plates (6 in. by 6 in. by 0.25 in). A two-pound steel weight (6.5 in. by 2 in. by 1.5 in.) was then placed on the upper plate to obtain 1.3 psi on each specimen. The laminate was conditioned in a drying oven for 24 hours at 125°F ± 5°. After removal from the oven, each sandwich combination was cooled for two hours, and was then tested for degree of blocking according to the following scale.

Degree N.B. -- No blocking. No adhesion between surfaces; coated fabrics slide freely.

Degree Sl.B. -- Slight blocking. Coated fabrics have to be peeled apart, but surfaces remain intact.

Degree B. -- Blocking. Coated fabrics have to be peeled apart, and surfaces are damaged.

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Procedure I: Preparation of Unplasticized Polyvinyl
              Chloride Films by the Solution-Casting Method

A 15% solution of unplasticized polyvinyl chloride (Geon
121 Paste Resin) was prepared by adding the powder to
warm solvent (Cyclohexanone 5104), with agitation. The
resultant, yellowish viscous solution was strained through
Fiberglas, and was allowed to cool. Films were cast from
the material by pouring the solution onto glass plates,
edged with glass strips. The solvent was allowed to evaporate
in air for fifteen to twenty hours.

Procedure J: Heat-Treating Unplasticized Polyvinyl
              Chloride Films Obtained by the Solution-
              Casting Method

Two films were cast from a 15% solution of unplasticized
polyvinyl chloride (Geon 121 Paste Resin) in cyclohexanone.
The films were air-dried for 15 hours, after which they were
placed in an oven at 70°C. for 4 hours and 8 hours, respec-
tively.

Procedure K: Preparation of Veloform Films by the Solution-
           Casting Method.

A 20% solution of Veloform P-10 in a 65/35 mixture of
methyl ethyl ketone and toluene was poured onto glass
plates, edged with strips of glass. The plates were set
aside for 15 hours to allow the solvent to evaporate.
No heat treatment was given the films.

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